Elements of Chemistry: Chemical physics

William Allen Miller, Herbert McLeod

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ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

BY
WILLIAM ALLEN MILLER, M.D., D.C.L., LL.D.

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PART III.

CHEMISTRY OF CARBON COMPOUNDS,
OR
ORGANIC CHEMISTRY.

SECTION I.

HYDROCARBONS, ALCOHOLS, ETHERS, ALDEHYDES AND PARAFFINOID ACIDS.

FIFTH EDITION.

LONDON:
LONGMANS, GREEN AND CO.
1880.

QD28
M5
1877
v.3

Ballantyne Press
BALLANTYNE AND HANSON, EDINBURGH
CHANDOS STREET, LONDON

PREFACE.

A COMPARISON of this edition with the previous one, published in 1869, will render it evident that the present volume is practically a New Treatise, more than four-fifths of the whole having been rewritten. The rapid development of that branch of chemical science which comprises the carbon compounds rendered a change necessary in the system of classification employed by the late Professor Miller, and the adoption of one based on the analogy in chemical constitution and properties of compounds rather than on the source from which they happen to be obtained. At first an attempt was made simply to rearrange and enlarge the work, so as to include the more important discoveries made since the issue of the last edition, but this had soon to be abandoned as impracticable. It therefore became necessary to rewrite the Treatise, incorporating those portions of the original which might be available for the purpose. The slight unevenness in the character of the work, which will be apparent on comparison of the first few chapters with the later ones, is chiefly due to this cause.

In this volume, the cyanides, the hydrocarbons and their haloid, nitro- and cyano-derivatives, the alcohols and thio-alcohols, the ethers, aldehydes, ketones, the quinones, and compounds more or less closely allied to one or other of these great groups—such as the carbohydrates and glucosides—are fully discussed. Only one section of the acids are described—namely, those belonging, for the most part, to what may conveniently be termed the *paraffinoid* (so-called fatty) group. The acids of the *benzenoid* (so-called aromatic) group, the nitrogen compounds of basic character, and the organo-metallic compounds, will form the chief subjects of a second volume, which will shortly be published.

It is hoped that the work will not only be found to contain a fairly complete account of the present state of knowledge of the groups above mentioned, but more especially that it will be of assistance to the advanced student, not merely in enabling him to acquire facts, but as a guide, both to the methods of inquiry which are of service in this branch of chemistry, and to the principles on which the theoretical deductions are based. As a rule, instead of simple dogmatic statements, the objections against any particular view are given, as well as the arguments in favour of it.

References to the original sources of information are freely introduced. In many cases, when only a single authority is quoted, it will be found on consulting the paper quoted that it contains a full account of, or reference to, the labours of other investigators. When the name of an author alone is appended to a particular statement, the paper in which the information is conveyed will in most cases be discovered without difficulty by consulting the Index to *Liebig's Annalen*, the *Jahresbericht*, the *Berichte*, or the *Chemical Society's Abstracts*. The Index, also, has been made as full and complete as possible. Several friends whose names are mentioned in the text have favoured us with important information, for which we desire here to record our warmest thanks.

It is evident that in a work of this size there must be many omissions, and the conclusions arrived at are in some cases more or less open to question; but it could scarcely be otherwise, on account of the very great extent of the literature to be discussed, and the difficulty consequent on this of properly taking into consideration, and fairly weighting, all the known statements of results. It must also not be forgotten that no comprehensive work on the subject has appeared since the publication of Kekulé's ever-memorable *Lehrbuch*, and therefore that the compilation of an extended treatise like the present is attended by many difficulties. We trust, however, that a solid foundation has been laid, and that the chief features of the modern chemistry of carbon compounds are truthfully pictured.

Notwithstanding the extraordinary increase in the number of the carbon compounds, their study is gradually becoming simplified as the possibility is extended of arranging them in series, and of giving a general description of their chief properties applicable to all the members of the group. For example, the principal laws which, in all probability, govern the formation of many hundred substitution derivatives of benzene may now be expressed in a few lines. We are not without hope that this volume may be of service in aiding the progress of our science, for at every step in the attempt to generalize difficulties arise owing to the imperfection of our records: important terms in a series of compounds are unknown, or the properties of members of the series are very imperfectly determined, or are obviously inaccurately stated; and consequently we are unable to draw conclusions with any confidence as to the behaviour of the series as a whole. Evidence of this will be found on page after page of the present volume, clearly showing that at no time more than the present was greater opportunity afforded for useful research, much of the work to be accomplished being of a kind well within the powers of an intelligent, but comparatively inexperienced student. It has been somewhat the fashion of late to decry the attention which is being paid to the investigation of carbon compounds, but this undoubtedly arises from an imperfect appreciation of the methods and objects of this department of chemistry. For a long time, the investigation of compounds other than those which contain carbon was carried on in the most desultory and unsatisfactory manner without any definite aim or object; now that the study of the carbon compounds has led chemists to the discovery of a series of beautifully simple relationships subsisting between them, the necessity of investigating the relationship between the remaining elements and their compounds is for the first time fully recognized. Mendeljeff's so-called periodic law may be regarded simply as an extension of the laws which govern the carbon compounds to the elements generally.

At the present time, what is most required is the accurate and complete examination of individual carbon compounds, for chemists have hitherto too often been satisfied if they simply prepared a given substance, analyzed it, and described a few of its reactions; a compound is seldom obtained in quantity sufficient to admit of its complete purification and the subsequent determination of its physical constants. These constants can be most advantageously determined by those who have the necessary apparatus at their command, and above all, special experience in such matters; and if each chemical school would make the preparation by its students of certain substances in a state of purity a part of the ordinary course of study, and would give notice that these particular compounds were at the disposal of experts for the determination of physical constants, much would be done to facilitate the study of a comparatively neglected branch of science. We have now reached a stage at which it is fully recognized that there is no definite limit between the physical and chemical properties of compound, and it is obvious that without a complete knowledge of both no material progress can be made.

Almost at the close of the volume we have briefly discussed the insufficiency of the present theory of isomerism, and have given a sketch of the Van't Hoff-Le Bel hypothesis, which is, we believe, worthy of the most careful consideration; for although it does not appear to meet all the difficulties, and may therefore eventually have to be modified or abandoned for a more comprehensive theory, its application to the study of isomerism in carbon compounds is certain to lead to discoveries of importance.

Finally, we would express the wish that our readers will have the kindness to point out any mistakes that they may notice, and we shall also gladly welcome any suggestions or information. It is requested that communications on these points be addressed to Dr. Armstrong.

HENRY E. ARMSTRONG.
CHARLES E. GROVES.

June, 1880.

TABLE OF CONTENTS.

CHAPTER I.

NO. OF PARAGRAPH PAGE

Introductory—Analysis of Carbon Compounds —Molecular Formulæ . . . . 1—41

§ I. Introductory.

1025 Definition of Organic Chemistry 1

§ II. Analysis of Carbon Compounds.

1026 Analysis of Carbon Compounds 3
1027 Proximate Analysis . . . . ib.
1028 Separation by Solvents 4
1029 Fractional Crystallization and Fractional Solution . . 6
1030 Fractional Precipitation and Fractional Saturation . . ib.
1031 Fractional Distillation 7, 1000
1032 Ultimate Analysis 11, 1000
1033 Determination of Carbon, Hydrogen and Nitrogen . . 12
1034 Analysis of a Solid not containing Nitrogen . . . 13
1035 Analysis of a Liquid not containing Nitrogen . . . 21
1036 Analysis of a Body containing Nitrogen 22
1037 Method of Varrentrapp and Will 23
1038 Method of Dumas 25
1039 Method of Relative Volumes 26
1040 Determination of Sulphur, Phosphorus and Arsenicum . ib.
1041 Determination of Chlorine, Bromine and Iodine . . 28, 1000
1042 Determination of other Elements 29
1043 Discrimination of the Gases . . . . ib.
1044 Arrangement of Gases into Analytical Groups . . . ib.
1045 Gases absorbable by Potassic Hydrate and non-inflammable . 30
1046 Gases absorbable by Potassic Hydrate and inflammable . ib.
1047 Gases not absorbable by Potassic Hydrate and non-inflammable 31
1048 Gases not absorbable by Potassic Hydrate and inflammable . ib.
1049 General Principles of the Analysis of a Mixture of Gases . 32
1050 Calculation of Analyses 35

NO. OF PARAGRAPH PAGE

§ III. Molecular Formulæ.

1051 Molecular Formulæ 36, 1000
1052 Hofmann's Method for Vapour Densities . . . . *ib.*
1053 Use of Vapour Density in determining Molecular Formulæ . 38
1054 Molecular Formulæ of non-volatile Compounds . . . 39
1055 Polymeric, Metameric and Isomeric Compounds . . . 40

CHAPTER II.

Quantivalence—Classification of Carbon Compounds—Theory of Compound Radicles. 42—71

§ I. Quantivalence.

1056 Quantivalence 42
1057 Atoms and Molecules 43
1058 Graphic Formulæ 44
1059 Varying Valency 47

§ II. Classification of Carbon Compounds.

1060 Combinations of Carbon and Hydrogen 49
1061 Hydrocarbons 50
1062 Haloid Derivatives of the Hydrocarbons 52
1063 Cyano-derivatives of the Hydrocarbons . . . . *ib.*
1064 Nitro-derivatives of the Hydrocarbons . . . . *ib.*
1065 Alcohols 53
1066 Thioalcohols or Mercaptans 54
1067 Chlorhydrins, Bromhydrins, &c.. . . . . . . *ib.*
1068 Ethers 55
1069 Thioethers . . . . *ib.*
1070 Aldehydes . . . . *ib.*
1071 Acids 56
1072 Carboxylic Acids or Carbo-acids . . . . . . *ib.*
1073 Sulphonic Acids or Sulpho-acids. 57
1074 Sulphinic Acids . . . . *ib.*
1075 Phosphonic Acids . . . . *ib.*
1076 Metallic Salts 58
1077 Haloid Salts . . . . *ib.*
1078 Ethereal Salts 59
1079 Acid Chlorides, Bromides and Iodides . . . . . *ib.*
1080 Acid Amides . . . . *ib.*
1081 Haloid Derivatives of the Acids 60
1082 Acid Anhydrides . . . . *ib.*
1083 Ketones . . . . *ib.*
1084 Amines and Allied Compounds 61
1085 Organo-Metallic Compounds 63

NO. OF PARAGRAPH PAGE

§ III. Theory of Compound Radicles.

1086 Compound Radicles 64
1087 Chemical Types 67

CHAPTER III.

Action of Reagents on Carbon Compounds 71—87

1088 Action of Oxidizing Agents 71
1089 Action of Nascent Hydrogen 75
1090 Action of the Halogens 78
1091 Action of Haloid Compounds of Phosphorus . . . 81
1092 Action of Hydrochloric, Hydrobromic and Hydriodic Acids 82
1093 Action of Nitric Acid and of Nitrous Acid . . . . ib.
1094 Action of Dehydrating Agents 83
1095 Action of Alkaline Reagents 85
1096 Use of Acetic Chloride and of Benzonic Chloride . . 86
1097 Other Reagents and Agents . . . . . . ib.

CHAPTER IV.

Cyanogen and its Compounds . . . 87—126

1098 Cyanogen 87
1099 Paracyanogen 89
1100 Hydrocyanic Acid 90, 1000
1101 Compounds of Hydrocyanic Acid with Haloid Acids . . 94
1102 Trihydrocyanic Acid . . . . ib.
1103 Detection of Hydrocyanic Acid and the Cyanides . . ib.
1104 Estimation of Hydrocyanic Acid 95
1105 Cyanides 96
1106 Potassic Cyanide . . . . ib.
1107 Double Cyanides 98
1108 Double Cyanides 99
1109 Argentic Cyanide . . . . ib.
1110 Mercuric Cyanide 100
1111 Cyanides of Gold 101
1112 Cyanides of Iron 102
1113 Ferrocyanides and Ferricyanides . . . . . ib.
1114 Potassic Ferrocyanide . . . . ib.
1115 Other Ferrocyanides 104
1116 Hydroferrocyanic Acid . . . . ib.
1117 Potassic Ferricyanide 105
1118 Hydroferricyanic Acid 107
1119 Prussian Blue . . . . ib.

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NO. OF PARAGRAPH		PAGE
1120	Ferrous Dipotassic Ferrocyanide	107
1121	Diferrous Dipotassic Ferricyanide	107, 1000
1122	Triferrous Ferricyanide—Commercial Prussian Blue	109
1123	Nitroprussides	110
1124	Composition of the Nitroprussides	111
1125	Hydronitroprussic Acid	*ib.*
1126	Sodic Nitroprusside	*ib.*
1127	Cobaltocyanides and Cobalticyanides	*ib.*
1128	Manganocyanides and Manganicyanides	112
1129	Chromicyanides	*ib.*
1130	Osmiocyanides and Rutheniocyanides	113
1131	Platinocyanides	*ib.*
1132	Platinicyanides	114
1133	Palladiocyanides	*ib.*
1134	Rhodicyanides and Iridicyanides	115
1135	Chlorides of Cyanogen	*ib.*
1136	Bromides of Cyanogen—Iodide of Cyanogen	116
1137	Cyanic Acid	*ib.*
1138	Potassic Cyanate—Potassic Isocyanate	117
1139	Sulphocyanates or Thiocyanates	118
1140	Sulphocyanic Acid	120
1141	Sulphocyanic Anhydride	*ib.*
1142	Persulphocyanic Acid	*ib.*
1143	Persulphocyanogen	*ib.*
1144	Dicyanic Acid	121
1145	Cyanuric Acid	*ib.*
1146	Constitution of Cyanic and Cyanuric Acids	122
1147	Cyanilic Acid	123
1148	Fulminates	*ib.*
1149	Argentic Fulminate	*ib.*
1150	Mercuric Fulminate	124
1151	Fulminuric Acid	125

CHAPTER V.

The Hydrocarbons and their Haloid, Nitro- and Cyano-Derivatives . . 126—402

§ I. Hydrocarbons of the C_nH_{2n+2} Series.

The Paraffins.

1152	Paraffins	126
1153	Methods of Formation of the Paraffins	127
1154	Constitution of the Paraffins	130
1155	Isomerism in the Paraffin Series	132

NO. OF PARAGRAPH		PAGE
1156	Methane or Marsh Gas	133
1157	Ethane	137
1158	Propane	138
1159	Tetrane or Butane	*ib.*
1160	Pentane	139
1161	Hexane	*ib.*
1162	Heptane	140, 1000
1163	Higher Homologues of Methane	140
1164	Paraffin	141
1165	Bitumen, Asphalt and Petroleum	146
1166	Action of Haloids on the Paraffins	147, 1000
1167	Preparation of Haloid Derivatives of the Paraffins	147
1168	Haloid Derivatives of Methane	151
1169	Monochloromethane or Methylic Chloride	*ib.*
1170	Dichloromethane or Methylenic Chloride	*ib.*
1171	Trichloromethane or Chloroform	151, 1000
1172	Tetrachloromethane or Carbonic Tetrachloride	153
1173	Bromomethanes	*ib.*
1174	Iodomethanes	154
1175	Haloid Derivatives of Ethane	155, 1001
1176	Chlorethanes—Ethylic Chloride—Ethylenic Chloride—Ethylidenic Chloride	155
1177	Monobromethane or Ethylic Bromide	156
1178	Dibromethanes—Ethylenic Bromide—Ethylidenic Bromide	*ib.*
1179	Iodethane or Ethylic Iodide	157
1180	Iodochlorethane and Iodobromethane	*ib.*
1181	Diiodethanes—Ethylenic Iodide—Ethylidenic Iodide	158
1182	Haloid Derivatives of Propane—Monochloropropanes	*ib.*
1183	Dichloropropanes	*ib.*
1184	Trichloropropanes	159
1185	Tetrachloropropanes	*ib.*
1186	Hexachloropropanes	*ib.*
1187	Bromopropanes	*ib.*
1188	Dibromopropanes	159, 1001
1189	Chlorobromopropanes	160
1190	Tribromopropanes	*ib.*
1191	Tetrabromopropanes	*ib.*
1192	Chlorobromopropanes	*ib.*
1193	Iodopropanes	*ib.*
1194	Chloriodopropanes	161
1195	Haloid Derivatives of the Tetranes	*ib.*
1196	Haloid Derivatives of the Pentanes	162
1197	Haloid Derivatives of the remaining Paraffins	*ib.*
1198	Haloid Derivatives of the Hexanes	*ib.*
1199	Haloid Derivatives of the Heptanes	163

NO. OF PARAGRAPH PAGE
1200 Haloid Derivatives of Octane . . . 163
1201 Haloid Derivatives of Hexadecane . . . ib.
1202 Mononitro-paraffins . . . 164, 1001
1203 Ethylnitrolic Acid . . . 168
1204 Action of Nitrous Acid on Secondary Nitro-paraffins . . . ib.
1205 Trinitromethane or Nitroform . . . 169
1206 Tetranitromethane . . . ib.
1207 Dinitropropane . . . 169, 1001
1208 Trinitroproprane . . . 169
1209 Haloid Derivatives of Nitroparaffins . . . ib.
1210 Chloronitromethane . . . 170
1211 Trichloronitromethane or Chloropicrin . . . ib.
1212 Dichlorodinitromethane . . . ib.
1213 Bromotrinitromethane . . . ib.
1214 Trichlorodibromonitroethane—Trichlorotrinitroethane . . . ib.
1215 Tribromonitromethane or Bromopicrin . . . ib.
1216 Cyano-derivatives of the Paraffins . . . 171
1217 Monocyanoparaffins . . . 172
1218 Properties of the Cyanoparaffins or Nitriles . . . 173
1219 Properties of the Isocyanides or Carbamines . . . 174
1220 Higher Cyano-derivatives of the Paraffins . . . 175, 1001
1221 Haloid Derivatives of the Cyano-paraffins . . . 176
1222 Constitution of the Fulminates . . . ib.
1223 Fulminuric Acid . . . 177

§ II. Hydrocarbons of the C_nH_{2n} or Olefine Series.

1224 Olefines . . . ib.
1225 Methods of Formation of the Olefines . . . 178
1226 Properties of the Olefines . . . 180, 1001
1227 Isomerism of the Olefines . . . 182, 1001
1228 Ethylene or Olefiant gas . . . 183
1229 Polymerization of Ethylene . . . 190
1230 Propylene . . . ib.
1231 Butylene . . . 191, 1001
1232 Amylene . . . 193, 1001
1233 Hexylene . . . 195, 1001
1234 Heptylene . . . 196, 1001
1235 Octylene . . . 197, 1002
1236 Nonylene . . . 197
1237 Decylene . . . ib.
1238 Other Olefines . . . 198
1239 Haloid Derivatives of the Olefines . . . 199, 1002
1240 Chlorethylenes . . . 200
1241 Bromethylenes . . . 201

NO. OF PARAGRAPH PAGE
1242 Iodethylenes 202
1243 Chloropropylenes 203
1244 Bromopropylenes 205, 1002
1245 Iodopropylenes 207
1246 Haloid Derivatives of other Olefines 208

§ III. Hydrocarbons of the C_nH_{2n-2} or Acetylene Series.

1247 Hydrocarbons of the Acetylene Series . . . . . ib.
1248 Acetylene 209, 1002
1249 Metallic Derivatives of Acetylene 214, 1002
1250 Homologues of Acetylene 215
1251 Constitution of the Homologues of Acetylene . . . 216
1252 Allylene—Isoallylene . . . . . . , . . 217
1253 Crotonylene 218
1254 Propylacetylene—Isopropylacetylene—Valerylene—Isoprene 219, 1002
1255 Hexoylene—Diallyl 220, 1002
1256 Amylacetylene—Tetramethylallene 221
1257 Caprylidene—Tetrahydrometaxylene . . . . . ib.
1258 Decenylene—Menthene—Rutylene . . . . . ib.
1259 Endecenylene 222
1260 Benylene . . . . ib.
1261 Cetenylene . . . . ib.

§ IV. Hydrocarbons of the C_nH_{2n-4} Series.

1262 Terpenes 222, 1002
1263 Valylene 223
1264 Caprene 224
1265 Artificial Terpenes 224, 1002
1266 Natural Terpenes 225
1267 French Turpentine Oil—Terebenthene 226
1268 Compounds of Terebenthene with the Haloid Acids . 227, 1002
1269 Polymerization of Terebenthene 229
1270 Isoterebenthene 230
1271 Terebene 231, 1002
1272 Camphenes 232
1273 Terpene from Isoprene 234
1274 English Turpentine Oil—Austraterebenthene . . . ib.
1275 Substitution Derivatives of the Terpenes . . . 235, 1003
1276 Compounds of the Terpenes with Water . . . 236, 1003
1277 Behaviour of the Terpenes on Oxidation 237
1278 Terpenes from other Sources—Essential Oils . . . 238
1279 Caoutchouc or Indian Rubber 243
1280 Vulcanized Indian Rubber 244
1281 Gutta Percha 245

NO. OF PARAGRAPH PAGE

§ V. Hydrocarbons of the C_nH_{2n-6} or Benzene Series.

1282 Products of the Distillation of Coal 247
1283 Manufacture of Coal Gas 248
1284 Compounds present in Coal-tar 251, 1003
1285 Products of the Distillation of Cannel Coal and Lignite . 254
1286 Products of the Distillation of Wood . . . . . ib.
1287 Stockholm Tar 255
1288 Creasote . . . . ib.
1289 Distillation of Peat 257
1290 Products of the Distillation of Menhaden Oil Soap . . ib.
1291 Products of the Distillation of Bones 258, 1003
1292 Benzene or Benzol 258, 1003
1293 Dipropargyl 275
1294 Homologues of Benzene 276, 1003
1295 Behaviour of the Homologues of Benzene on Oxidation . 279
1296 Action of Hydrogen on the Homologues of Benzene . . 281
1297 Action of the Halogens on the Homologues of Benzene . ib.
1298 Action of Nitric and Sulphuric Acids on the Homologues of Benzene 283
1299 Toluene or Methylbenzene . . . . ib.
1300 Ethylbenzene—Xylenes 284, 1003
1301 Hydrocarbons C_9H_{12}—Cumene—Mesitylene, &c. . . 286, 1003
1302 Hydrocarbons $C_{10}H_{14}$—Cymene—Durene, &c. . . 287, 1003
1303 Hydrocarbons $C_{11}H_{16}$—Amylbenzene—Laurene, &c. . . 295
1304 Hydrocarbons $C_{12}H_{18}$ 295, 1003
1305 Hydrocarbons $C_{13}H_{20}$ 296
1306 Hydrocarbons $C_{15}H_{24}$—Essential Oils 297, 1004
1307 Haloid Derivatives of Benzene and its Homologues . . 298
1308 Benzene Hexabromide 300
1309 Bromobenzene or Phenylic Bromide . . . . . . ib.
1310 Dibromobenzenes . . . . ib.
1311 Tribromobenzenes 302
1312 Tetrabromobenzenes 305
1313 Pentabromobenzenes, Hexabromobenzene . . . 305, 1004
1314 Benzene Hexachloride 305
1315 Chlorobenzene or Phenylic Chloride . . . . . . ib.
1316 Dichlorobenzenes 307
1317 Trichlorobenzenes 309, 1004
1318 Tetrachlorobenzenes . . . . ib. ib.
1319 Pentachlorobenzene 309
1320 Hexachlorobenzene . . . . ib.
1321 Fluorbenzene 310
1322 Iodobenzene or Phenylic Iodide 310, 1004
1323 Diiodobenzene 311

NO. OF PARAGRAPH PAGE
1324 Triiodobenzene . . . 311
1325 Chlorobromobenzene . . . ib.
1326 Bromiodobenzenes . . . ib.
1327 Chloriodobenzenes . . . ib.
1328 Chloro-derivatives of Toluene . . . ib.
1329 Monochlorotoluenes—Benzylic Chloride . . . 313
1330 Dichlorotoluenes . . . 314
1331 Trichlorotoluenes . . . ib.
1332 Tetrachlorotoluenes . . . 316
1333 Pentachlorotoluenes . . . ib.
1334 Hexachlorotoluenes . . . 317
1335 Heptachlorotoluenes . . . ib.
1336 Chloro-derivatives of the Homologues of Toluene . . . 318
1337 Bromo-derivatives of Toluene . . . 319
1338 Bromoxylenes . . . 321
1339 Bromethylbenzene . . . ib.
1340 Bromotrimethylbenzene . . . ib.
1341 Bromo-derivatives of Higher Homologues of Benzene . . . 322
1342 Iodo-derivatives of the Homologues of Benzene . . . ib.
1343 Nitro-derivatives of the Benzene Series . . . ib.
1344 Nitrobenzene . . . 323, 1004
1345 Dinitrobenzenes . . . 324
1346 Nitrotoluenes . . . 324, 1004
1347 Nitroxylenes . . . 325
1348 Nitrotrimethylbenzenes . . . 326
1349 Cyano-derivatives of Benzene—Benzonitrile—Phenylcarbamine 327
1350 Cyano-derivatives of the Homologues of Benzene . . . 329
1351 Nitro-haloid Derivatives of Benzene and its Homologues . ib.
1352 Nitro-haloid Derivatives of Benzene . . . 330
1353 Nitro-haloid Derivatives of Toluene . . . 332, 1004
1354 Action of Alkalies on Nitro-haloid Derivatives of this Series . 333
1355 Action of Potassic Cyanide on Nitro-haloid Derivatives of this Series . . . 334
1356 General Review of the Action of Reagents on Benzene and its Homologues . . . 336, 1004

§ VI. Hydrocarbons of the C_nH_{2n-8} or Cinnamene Series.

1357 Cinnamene or Styrolene . . . 340, 1004
1358 Metacinnamene . . . 342
1359 α-Phenylpropylene or Methylphenylethylene . . . ib.
1360 β-Phenylpropylene or Allylbenzene . . . ib.
1361 α-Phenylbutylene or Ethylphenylethylene . . . ib.
1362 β-Phenylbutylene or Phenethylethylene—Naphthalene Tetrahydride . . . 343

NO. OF PARAGRAPH PAGE

§ VII. Hydrocarbons of the C_nH_{2n-10} or Acetenylbenzene Series.

1363 Acetenylbenzene or Phenylacetylene 343

§ VIII. Hydrocarbons of the C_nH_{2n-12} or Naphthalene Series.

1364 Naphthalene 345
1365 Constitution of Naphthalene . . . . . . , 346
1366 Isomeric Substitution Derivatives of Naphthalene . . 348
1367 Action of Chlorine on Naphthalene 351, 1004
1368 Bromonaphthalenes 353
1369 Moniodonaphthalene . . . . ib.
1370 Nitronaphthalenes . . . . ib.
1371 Cyanonaphthalenes 354
1372 Homologues of Naphthalene . . . . . . ib.

§ IX. Hydrocarbons of the C_nH_{2n-14} or Diphenyl Series.

1373 Diphenyl or Phenylbenzene 355
1374 Substitution Derivatives of Diphenyl 356
1375 Acenaphthene 357
1376 Homologues of Diphenyl; Mode of Formation . . 358, 1004
1377 Diphenylmethane 360
1378 Hydrocarbons $C_{14}H_{14}$—Ditolyl, Dibenzyl, &c. . . . 361
1378*a* Hydrocarbons $C_{15}H_{16}$—Ditolylmethane, Dibenzylmethane, &c. 363
1379 Hydrocarbons $C_{16}H_{18}$—Ditolylethane, &c. . . . . . ib.
1380 Hydrocarbons $C_{19}H_{24}$—Dimesitylmethane . . . . ib.

§ X. Hydrocarbons of the C_nH_{2n-16} or Stilbene Series.

1381 Hydrocarbons of the Stilbene Series 364
1382 Acetylenenaphthalene or Acenaphthylene 365
1383 Fluorene—Stilbene—Isostilbene . . . . ib.
1384 Hydrocarbons $C_{14}H_{12}$—Dihydroanthracene 367
1385 Homologues of Stilbene 368

§ XI. Hydrocarbons of the C_nH_{2n-18} or Anthracene Series.

1386 Hydrocarbons of the Anthracene Series 370
1387 Anthracene . . . . ib.
1388 Action of Chlorine and Bromine on Anthracene . . . 373
1389 Constitution of Anthracene and its Derivatives . . 374, 1004
1390 Paranthracene 377
1391 Phenanthrene . . . . ib.

NO OF PARAGRAPH PAGE
1392 Constitution of Phenanthrene 379, 1004
1393 Tolane or Diphenylacetylene 381
1394 Methylanthracene 382
1395 Hydrocarbons $C_{16}H_{14}$—Dimethyltolane . . . . ib.
1396 Retene . . . . ib.

§ XII. Hydrocarbons of the C_nH_{2n-20} or Benzylnaphthalene Series.

1397 Hydrocarbons of the Benzylnaphthalene Series . . . 383

§ XIII. Hydrocarbons of the C_nH_{2n-22} or Pyrene Series.

1398 Hydrocarbons of the Pyrene Series . . . . . ib.
1399 Pyrene or Phenylene Naphthalene . . . . . ib.
1400 Diacetenylbenzene or Diphenyldiacetylene 385
1401 Paradiphenylbenzene . . . . ib.
1402 Triphenylmethane 385, 1004
1403 Hydrocarbons $C_{20}H_{18}$—Dibenzylbenzenes, &c. . . . 385
1404 Hydrocarbons $C_{21}H_{20}$ 386

§ XIV. Hydrocarbons of the C_nH_{2n-24} or Chrysene Series.

1405 Chrysene . . . . ib.
1406 Phenylenediphenylmethane 387

§ XV. Hydrocarbons of the C_nH_{n-26} or Dinapthyl Series.

1407 Dinaphthyl 388, 1004
1408 Isodinaphthyl 388
1409 Dinaphthylmethane 389

§ XVI. Hydrocarbons of the C_nH_{2n-28} Series.

1410 α-Dinaphthylethylene 389, 1004

§ XVII. Hydrocarbons of the C_nH_{2n-30} or Idrialene Series.

1411 Idrialene 390
1412 Triphenylbenzene . . . . ib.
1413 Tetraphenylmethane 390, 1004
1414 α-Tetraphenylethylene 390

§ XVIII. Hydrocarbons of the C_nH_{2n-32} or Tetraphenylethylene Series.

1415 Tetraphenylethylene 391

NO. OF PARAGRAPH PAGE

§§ XIX. & XX. Hydrocarbons of the C_nH_{2n-34} and C_nH_{2n-36} Series.

1416 General Review of the Hydrocarbons 391, 1004

CHAPTER VI.

The Alcohols . . . . . . 403—663

1417 General Character of the Alcohols 403

§ I. Alcohols of the C_nH_{2n+1} .OH or Ethylic Series.

1418 Alcohols of the Ethylic Series 404
1419 Classification of Alcohols 405, 1004
1420 Isomerism of the Alcohols of the Ethylic Series . . . 406
1421 Methods of Formation of Alcohols of the Ethylic Series, 407, 1004
1422 Diagnosis of Primary, Secondary and Tertiary Alcohols, 415, 1004
1423 General Properties of Alcohols of the Ethylic Series . . 415
1424 Behaviour of the Alcohols on Oxidation 416
1425 Other Reactions of Alcohols of the Ethylic Series . . 419
1426 Methylic Alcohol 422, 1005
1427 Ethylic Alcohol or Methylcarbinol—Wines and Fermented Liquors 425, 1005
1428 Propylic or Tritylic Alcohols 434
1429 Primary Propylic Alcohol or Ethylcarbinol . . . . ib.
1430 Secondary Propylic Alcohol or Dimethylcarbinol . . 435, 1005
1431 Butylic or Tetrylic Alcohols 438
1432 Normal Primary Butylic Alcohol or Propylcarbinol . . ib.
1433 Isoprimary Butylic Alcohol or Isopropylcarbinol . . . ib.
1434 Secondary Butylic Alcohol or Ethylmethylcarbinol . . 439
1435 Tertiary Butylic Alcohol or Trimethylcarbinol . . 439, 1005
1436 Amylic or Pentylic Alcohols 444
1437 Normal Primary Amylic Alcohol or Butylcarbinol . . 445
1438 Isoprimary Amylic Alcohols 445, 1005
1439 Secondary Amylic Alcohols 449, 1005
1440 Tertiary Amylic Alcohol or Ethyldimethylcarbinol . . 450
1441 Hexylic Alcohols 452
1442 Primary Hexylic Alcohols . . . . ib.
1443 Secondary Hexylic Alcohols . . . . ib.
1444 Tertiary Hexylic Alcohols 454, 1005
1445 Heptylic Alcohols 454
1446 Primary Heptylic Alcohols . . . . ib.
1447 Secondary Heptylic Alcohols 455
1448 Tertiary Heptylic Alcohols 455, 1005

NO. OF PARAGRAPH PAGE
1449 Octylic Alcohols 456
1450 Normal Primary Octylic Alcohol or Heptylcarbinol . . ib.
1451 Primary Hexylmethylcarbinol . . . . ib.
1452 Propyldiethlycarbinol 457
1453 Higher Homologues of Ethylic Alcohol . . . . ib.
1454 Relations between the Boiling Pcints of Alcohols of the Ethylic Series 457, 1005
1455 Haloid Derivatives of the Alcohols of the Ethylic Series . 461

§ II. Alcohols of the $C_nH_{2n-1}.OH$ or Allylic Series.

1456 Allylic Alcohol 464
1457 Allyldimethylcarbinol 466, 1005
1458 Menthylic Alcohol or Menthol 467

§ III. Alcohols of the $C_nH_{2n-3}.OH$ and $C_nH_{2n-5}.OH$ Series.

1459 Alcohols of the Propargylic Series . . . . . ib.
1460 Propargylic Alcohol . . . . ib.
1461 Diallylmethylcarbinol. 468, 1005

§ IV. Alcohols of the $C_nH_{2n-7}.OH$ Series.

1462 Alcohols derived from Hydrocarbons of the Benzene Series 469, 1005
1463 Methods of Preparing Phenols 470, 1005
1464 Methods of Preparing Alcohols of the Benzylic Series . . 471
1465 General Properties of the Phenols and Alcohols of the Benzylic Series 472
1466 Phenol 475, 1005
1467 Nitro-derivatives of Phenol. 476
1468 Nitrosophenol 477
1469 Amido- and Amidonitro-derivatives of Phenol . . . 478
1470 Sulphonic Acids derived from Phenol . . . . . ib.
1471 Haloid Derivatives of Phenol 480, 1005
1472 Haloid Derivatives of Nitrophenols 482
1473 Haloid Derivatives of Sulpho-, Nitrosulpho-, Amidosulpho- and Nitrosulpho-phenols 483
1474 Mode of Determining the Constitution of Phenol Derivatives 485
1475 Law of Substitution in the Phenol Series 489
1476 Alcohols of Composition $C_7H_7.OH$ 490
1477 Benzylic Alcohol or Phenylcarbinol . . . . . . ib.
1478 Cresol or Methylphenol 491
1479 Alcohols of the Composition $C_8H_9.OH$ 492, 1005
1480 Alcohols of the Composition $C_9H_{11}.OH$ . . . 494, 1005
1481 Alcohols of the Composition $C_{10}H_{13}.OH$. 494
1482 Sycocerylic Alcohol 495

NO. OF PARAGRAPH PAGE

§ V. Alcohols derived from Hydrocarbons Isologous with Benzene.

1483 Alcohols derived from Hydrocarbons of the Cinnamene Series 495, 1006
1484 Alcohols derived from Naphthalene 497
1485 Nitroso-, Nitro- and Amido-derivatives of the Naphthols . 499
1486 Constitution of the Naphthol Derivatives 501
1487 Alcohols of the Diphenyl Series 502
1488 Diphenylenecarbinol or Fluorene Alcohol 503
1489 Alcohols derived from Anthracene 504, 1006
1490 Triphenylcarbinol 504

§ VI. Dihydric Alcohols of the $C_nH_{2n}(OH)_2$ or Glycol Series.

1491 Glycols and Aldehydrols . . . . ib.
1492 Methods of Preparing Alcohols of the Glycol Series . . 505
1493 Classification of the Glycols 506
1494 Properties of the Glycols 507
1495 Methaldehydrol 509
1496 Glycol or Ethylenic Alcohol 509, 1006
1497 Polyethylenic Glycols 512
1498 Chloral Hydrate or Trichlorethaldehydrol 513
1499 Alcohols of the Composition $C_3H_6(OH)_2$ . . . 514, 1006
1500 Alcohols of the Composition $C_4H_8(OH)_2$ 515
1501 Alcohols of the Composition $C_5H_{10}(OH)_2$ 516
1502 Alcohols of the Composition $C_6H_{12}(OH)_2$ . . . 517, 1006
1503 Higher Homologues of Glycol 517
1504 Boiling points of the Glycols 519

§ VII. Dihydric Alcohols of the $C_nH_{2n-6}(OH)_2$ Series.

1505 Dihydric Alcohols derived from Hydrocarbons of the Benzene Series 519, 1006
1506 Dihydroxyl Derivatives of Benzene 521
1507 Resorcin or Resorcinol . . . . ib.
1508 Haloid Derivatives of Resorcinol 522, 1006
1509 Nitroso- and Nitro-derivatives of Resorcinol . . . 523
1510 Pyrocatechin or Catechol . . . . ib.
1511 Hydroquinone or Quinol 524
1512 Haloid Derivatives of Hydroquinone . . . . . ib.
1513 Constitution of the Dihydroxyl Derivatives of Benzene . 526
1514 Dihydroxyl Derivatives of Toluene 527
1515 Saligenin or Saligenol . . . . ib.
1516 Orcin or Orcinol . . . . ib.
1517 Constitution of Orcinol 530, 1006

NO. OF PARAGRAPH PAGE
1518 Haloid and Nitro-Derivatives of Orcinol 531
1519 Isomerides of Orcinol 532
1520 Alcohols of the Composition $C_8H_{10}(OH)_2$ 533
1521 Thymohydroquinone . . . . *ib.*

§ VIII. Dihydric Alcohols of Series higher than the $C_nH_{2n-8}(OH)_2$ Series.

1522 Hydronaphthaquinone or Naphthaquinol 534
1523 Dihydric Alcohols of the Diphenyl Series . . . . *ib.*
1524 Diphenols . . . . *ib.*
1525 Hydrobenzoin and Isohydrobenzoin 535, 1006
1526 Dithymol 536
1527 Anthrahydroquinone—Phenanthrenehydroquinone . 536, 1007
1528 Chrysenehydroquinone 537
1529 Dinaphthols . . . . *ib.*

§ IX. Trihydric Alcohols of the $C_nH_{2n-1}(OH)_3$ Series.

1530 Glycerin or Glycerol 537, 1007
1531 Polyglyceric Alcohols 546
1532 Amylic Glycerol 547

§ X. Trihydric Alcohols of the $C_nH_{2n-9}(OH)_3$ Series.

1533 Trihydric Alcohols of the Benzene Series . . . . *ib.*
1534 Pyrogallol 547, 1007
1535 Phloroglucin or Phloroglucol 550, 1007
1536 Trioxymetaxylene 552
1537 Phenylglycerol . . . . *ib.*
1538 Trioxycymene . . . . *ib.*
1539 Trioxynaphthalene . . . . *ib.*

§ XI. Tetrahydric Alcohols.

1540 Erythrite or Erythrol 553
1541 Naphthalene Alcohol or Naphtherythrol 554

§ XII. Pentahydric Alcohols.

1542 Quercite or Quercitol . . . . *ib.*
1543 Pinite 555
1544 Isodulcite 555, 1007

NO. OF PARAGRAPH PAGE

§ XIII. Hexahydric Alcohols.

1545 Mannite or Mannitol 556
1546 Dulcite or Dulcitol 558
1547 Sorbite 559
1548 Phenose . . . . ib.
1549 Inosite or Inosol 560
1550 Dambose 561
1551 Hexoxydiphenyl 562
1552 General Review of the Alcohols . . . . . ib.

The Carbohydrates.

1553 Carbohydrates 567
1554 Determination of the Cupric Oxide reducing power of Soluble Carbohydrates 568, 1007
1555 Determination of the Specific Rotatory Power of Optically Active Substances 569
1556 Sucrodextrose or Glucose 577
1557 Sucrodextroses from various sources 582
1558 Sucrolævulose or Lævulose 584
1559 Lactose or Galactose 585, 1008
1560 Arabinose or Pectinose 589
1561 Sorbinose or Sorbin . . . . ib.
1562 Eucalyptose or Eucalyn 590
1563 Artificial Glucoses . . . . ib.
1564 Saccharon or Cane Sugar 593, 1008
1565 Lacton or Milk Sugar 609, 1008
1566 Amylon, Starch Sugar or Maltose 612, 1008
1567 Mycon, Mycose or Trehalose 613
1568 Meleziton or Melezitose 614
1569 Eucalypton or Melitose 615
1570 Artificial Saccharons 615, 1008
1571 Starch or Fecula 616, 1008
1572 Paramylon 635
1573 Synanthrose 636
1574 Inulin 637
1575 Glycogen 641, 1009
1576 Cellulose 645
1577 Arabin, Metarabin, Pararabin 651
1578 Constitution of the Carbohydrates, Nomenclature . . 654
1578*a* Thio-alcohols or Mercaptans 659
1579 Thioethylic Alcohol or Mercaptan 661
1580 Thiophenol or Phenylic Sulphydrate 662
1581 Thiobenzylic Alcohol or Benzylic Sulphydrate . . . ib.

NO. OF PARAGRAPH PAGE

1582 Thionaphthols 662
1583 Thioglycol . . . . ib.
1584 Thioresorcinol—Thioquinol 663
1585 Thioglycerol . . . . ib.

CHAPTER VII.

Ethers. . . . 663—714

§ I. The Ethers.

1585a Preparation and Properties of the Ethers 663
1586 Methylic Oxide or Ether 667
1587 Ethylic Oxide or Ether 668
1588 Chlorinated Derivatives of Ethylic Ether 671
1589 Ethers of the $(C_nH_{2n-1})_2O$ and $C_nH_{2n+1}.O.C_nH_{2n-1}$ Series 673, 1009
1590 Ethers of the $C_nH_{2n+1}.O.C_nH_{2n-3}$ Series 673
1591 Ethers of the $(C_nH_{2n-7})_2O$ and $C_nH_{2n+1}.O.C_nH_{2n-7}$ Series—Phenylic Ether 674
1592 Methylphenylether or Anisol . . . . i.
1593 Benzyl Ethers 675
1594 Anethol 675, 1009
1595 Ethers derived from Polyhydric Alcohols—Ethylenic Oxide. 676
1596 Homologues of Ethylenic Oxide 678, 1009
1597 Glyceric Ether or Allylic Trioxide 679
1598 Mixed Ethers derived from Polyhydric and Monohydric Alcohols . . . . ib.
1599 Ethers derived from the Orcinols and Alcohols of the Ethylic Series 681

§ II. Ether Alcohols.

1600 Glycide 682
1601 Ether Alcohols derived from Dihydric Alcohols of the $C_nH_{2n}(OH)_2$ Series 683
1602 Ether Alcohols derived from Dihydric Alcohols of the $C_nH_{2n-6}(OH)_2$ Series—Guaiacol—Creosol . . . . ib.
1603 Eugenol 684
1604 Ether Alcohols derived from Glycerol 685
1605 Ether Alcohols derived from Pyrogallol 685, 1009

§ III. The Glucosides.

1606 Glucosides 686, 1006

NO. OF PARAGRAPH PAGE

§ IV. Thioethers and Polysulphides, Selenides and Tellurides.

1607 Thioethers—Preparation and Properties 704
1608 Ethylic Sulphide or Thioethylic Ether 706
1609 Higher Sulphides of Ethyl 708
1610 Homologues of Ethylic Sulphide . . . . . . ib.
1611 Compounds formed by the Union of Thioethers with the Moniodoparaffins 709
1612 Compounds formed by the Union of Thioethers with Dihaloid Paraffin Derivatives 711
1613 Allylic Sulphide . . . . ib.
1614 Phenylic Sulphides . . . . ib.
1615 Phenylenic Sulphides 712
1616 Benzylic Sulphide . . . . ib.
1617 Ethylenic Sulphide . . . . ib.
1618 Selenium Ethers 713
1619 Tellurium Ethers 714

CHAPTER VIII.

Aldehydes . . . . . . 714—770

1620 Aldehydes 714
1621 Formation of the Aldehydes 715
1622 General Properties of the Aldehydes 716

§ I. Aldehydes of the Acetic Series.

1623 List of Aldehydes of the Acetic Series 722
1624 Methaldehyde or Methylic Aldehyde 723
1625 Ethaldehyde or Aldehyde 727
1626 Polymerization of Ethaldehyde—Paraldehyde—Metaldehyde 731
1627 Condensation of Ethaldehyde 732
1628 Action of Chlorine and Bromine on Ethaldehyde . . . 733
1629 Combinations of Ethaldehyde with Acid Sulphites . . 734
1630 Ethaldehydrol Chloracetin or Chlorethylic Acetate . . 736
1631 Cyanethylic Alcohol . . . . ib.
1632 Trigenic Acid . . . . ib.
1633 Action of Ammonia and of Amines on Ethaldehyde . . 737
1634 Compounds formed from Aldehyde Ammonia . . 737, 1010
1635 Action of Ethaldehyde on Acid Amides 740
1636 Action of Aldehyde on Hydrocarbons 741
1637 Parathioethaldehyde 742
1638 Haloid Derivatives of Ethaldehyde—Chloral—Bromal . ib.
1639 Higher Homologues of Ethaldehyde 747

NO. OF PARAGRAPH PAGE
1640 Propaldehyde or Propylic Aldehyde 747
1641 Tetraldehydes . . . . *ib.*
1642 Tetraldol, Oxybutyric Aldehyde or Aldol 748
1643 Trichlorotetraldehyde or Trichlorobutyric Aldehyde . . 749
1644 Isotetraldehyde or Isobutyric Aldehyde . . . . *ib.*
1645 Pentaldehydes—Valeral 750
1646 Hexaldehydes 751
1647 Normal Heptaldehyde or Oenanthol 751, 1010
1648 Hexadecaldehyde or Cetylic Aldehyde . . . . *ib.*

§ II. Aldehydes of the C_nH_{2n-1}.COH or Acrylic Series.

1649 Acraldehyde or Acroleïn 752
1650 Crotonaldehyde 754

§ III. Aldehydes of the C_nH_{2n-7}.COH or Benzoic Series.

1651 Benzaldehyde or Benzoic Aldehyde 755
1652 Thiobenzaldehydes 759
1653 Haloid and Nitro-derivatives of Benzaldehyde . . . *ib.*
1654 Hydroxyl Derivatives of Benzaldehyde—Phenaldols . . 760
1655 Orthoxybenzaldehyde or Salicylic Aldehyde . . . *ib.*
1656 Paroxybenzoic Aldehyde 763
1657 Anisaldehyde, Paramethoxybenzoic or Anisic Aldehyde . *ib.*
1658 Parametadioxybenzaldehyde or Protocatechuic Aldehyde 764, 1010
1659 Paroxymetamethoxybenzaldehyde or Vanillin . . . 764
1660 Parametamethylenebenzaldehyde or Piperonal . . . 765
1661 Homologues of Benzaldehyde 765, 1010

§ IV. Monaldehydes of other Series.

1662 Furfuraldehyde or Furfurol 766, 1010
1663 Fucusaldehyde or Fucusol 767
1664 Cinnamic or Phenylacrylic Aldehyde . . . . . *ib.*
1665 Diphenethaldehyde 768
1666 Naphthoic Aldehydes 770, 1010

§ V. Dialdehydes.

1667 Oxalic Aldehyde or Glyoxal . . . . *ib.*
1668 Succinic Aldehyde 770
1669 Phthalic Aldehyde 770, 1010
1670 Terephthalic Aldehyde 770

NO. OF PARAGRAPH PAGE

CHAPTER IX.

The Ketones . . . . . 770—815

1671 Formation of Ketones 771, 1010
1672 Properties of Ketones 774, 1010

§ I. Ketones of the $CO(C_nH_{2n-1})_2$ Series.

1673 Dimethyl Ketone or Acetone 778
1674 Haloid Derivatives of Dimethyl Ketone 781
1675 Homologues of Dimethyl Ketone 783
1676 Methyl Tertiary-butyl Ketone or Pinacolin . . . ib.
1677 Methyl Nonyl Ketone . . . . ib.
1678 Table of the known Ketones of this Series . . . 783, 1010

§ II. Ketones of the $CO\left\{\begin{matrix}C_nH_{2n+1}\\C_nH_{2n-7}\end{matrix}\right.$ and $CO(C_nH_{2n-7})_2$ Series.

1679 Ketones of the $C_nH_{2n+1}.CO.C_nH_{2n-7}$ Series 785
1680 Ketones of the $CO(C_nH_{2n-7})_2$ Series 786

§ Ketones of other Series—Camphor.

1681 Naphthyl Ketones 787
1682 Mesityl Oxide 788
1683 Methyl Cinnamyl Ketone 789
1684 Phorone . . . . ib.
1685 Ethylene Diethyl Ketone—Phenylene Diethyl Ketone . . ib.
1686 Diphenylene Ketone . . . . ib.
1687 Camphor 790, 1010

§ IV. Quinones.

1687a Quinones 793
1688 Quinone or Benzoquinone 794
1689 Quinhydrone 797, 1010
1690 Phenoquinone . . . . ib. ib.
1691 Resorquinone 798
1692 Toluquinone or Methylquinone . . . . . . ib.
1693 Xyloquinone . . . . ib.
1694 Oxymetaxyloquinone . . . . ib.
1695 Cymoquinone or Thymoquinone . . . . . . ib.
1696 Oxycymoquinone 799
1697 Naphthaquinone . . . . ib.
1698 β-Naphthaquinone 800
1699 Coerulignone or Cedriret 800, 1010

NO. OF PARAGRAPH PAGE
1700 Tetroxydiphenoquinone 800
1701 Ethenedicymoquinone . . . . *ib.*
1702 Anthraquinone 801
1703 Monoxy-derivatives of Anthraquinone 802
1704 o–1 : 2 Dioxyanthraquinone or Alizarin . . . . *ib.*
1705 Isomerides of Alizarin—Purpuroxanthin—Anthraflavic acid, Chrysazin, Anthraflavone, &c. 804, 1011
1706 Trioxy-derivatives of Anthraquinone—Purpurin—Isopurpurin, &c. 805
1707 Tetroxy- and Hexoxy-derivatives of Anthraquinone . . 807
1708 Methylanthraquinone . . . . *ib.*
1709 Dimethylanthraquinone 808
1710 Constitution of Anthraquinone and its Oxy-derivatives 809, 1011
1711 Phenanthraquinone 811, 1011
1712 Pyrenequinone 811
1713 Dioxyretistene . . . . *ib.*
1714 Chrysoquinone 812
1715 Constitution of the Quinones 812, 1011

§ V. Sulphines and Sulphones.

1716 Dimethylsulphine, &c. 814
1717 Phenylsulphine . . . . *ib.*
1718 Dimethylsulphone, &c. . . . . *ib.*
1719 Diphenylsulphone, or Sulphobenzid 815

CHAPTER X.

The Acids and their more immediate Derivatives . . . . 816—999

1719*a* Acids 816
1720 Methods of Formation of Acids 817
1721 General Properties of Acids 818

§ I. Acids of the C_nH_{2n+1}.COOH or Acetic Series.

1722 Acids of the Acetic Series 820
1723 Formic or Methylic Acid 821, 1011
1724 Acetic or Ethylic Acid 824
1725 Propionic, Propylic or Methacetic Acid 828
1726 Tetrylic or Butyric Acids 829
1727 Pentylic or Valeric Acids 830
1728 Hexylic or Caproic Acids 833

NO. OF PARAGRAPH PAGE
1729 Heptylic or Œnanthylic Acid 834, 1011
1730 Octylic or Caprylic Acids 835
1731 Nonylic Acids 836
1732 Higher Homologues of Acetic Acid 836, 1012
1733 Decylic, Capric or Rutic Acid 837
1734 Lauric Acid 838
1735 Myristic Acid . . . . *ib.*
1736 Palmitic Acid 838
1737 Margaric Acid . . . . *ib.*
1738 Stearic Acid 839
1739 Arachidic Acid . . . . *ib.*
1740 Behenic Acid . . . . *ib.*
1741 Hyænic Acid . . . . *ib.*
1742 Cerotic Acid 840
1743 Melissic Acid—Boiling points of Acids of the Acetic Series . *ib.*
1744 Ethereal Salts of Acids of the Acetic Series—Modes of Formation 841, 1012
1745 Ethereal Salts derived from Acids of the Acetic Series, and Monohydric Alcohols 846
1746 Ethylic Formate 847
1747 Methylic Acetate . . . . *ib.*
1748 Ethylic Acetate 848
1749 Halogen Salts of Acids of the Acetic Series . . . 849
1750 Chlorine Acetate . . . . *ib.*
1751 Bromine Acetate 850
1752 Iodine Triacetate . . . . *ib.*
1753 Cyanogen Acetate . . . . *ib.*
1754 Thioacids of the Acetic Series—Thiacetic Acid . . . 851
1755 Acid Halides of the Acetic Series . . . . . . *ib.*
1756 Acetic Chloride, or Chloride of Acetyl—Acetic Bromide—Acetic Iodide 852
1757 Acetic Cyanide or Cyanide of Acetyl 853
1758 Acid Oxides or Anhydrides of the Acetic Series . . . *ib.*
1759 Acetic Oxide or Anhydride 855
1760 Trimethacetic Anhydride 856
1761 Acetic Thianhydride . . . . *ib.*
1762 Acetic Peroxide . . . . *ib.*
1763 Acetic Disulphide . . . . *ib.*
1764 Haloid Derivatives of Acids of the Acetic Series . . 857
1765 Chloracetic Acids 858
1766 Bromacetic Acids 859
1767 Iodacetic Acids 860
1768 Cyanacetic Acid . . . . *ib.*
1769 Haloid Derivatives of Propionic Acid . . . . . *ib.*
1770 Haloid Derivatives of Higher Acids 863

NO. OF PARAGRAPH PAGE

§ II. Amido- and Hydroxy-acids derived from Acids of the Acetic Series.

1771 Amido-Acids or Glycines 864
1772 Glycine, Glycocine or Amidacetic Acid 866
1773 Di- and Triglycolamidic Acids 867
1774 Hippuric or Benzamidacetic Acid and Allied Compounds . *ib.*
1775 Alanines or Propaneglycines 868
1776 Tyrosine 869
1777 Tetraneglycines . . . . *ib.*
1778 Pentaneglycines . . . . *ib.*
1779 Leucines or Hexaneglycines 870
1780 Octaneglycines . . . . *ib.*
1781 Hydroxy-acids derived from Acids of the Acetic Series . 871
1782 Acids of the Lactic Series 873
1783 Mode of Formation of Acids of the Lactic Series . . *ib.*
1784 Properties of Acids of the Lactic Series 875
1785 Hydroxyformic, or Carbonic Acid 876
1786 Metallic and Ethereal Carbonates . . . . . . *ib.*
1787 Compounds formed by the Displacement of one of the OH Groups in Carbonic Acid 878
1788 Ethereal Chlorocarbonates . . . . *ib.*
1789 Ethylic Cyanoformate or Cyanocarbonate . . . . *ib.*
1790 Amidoformic or Carbamic Acid and its Salts . . . 879
1791 Thiocarbonic Acids and their Derivatives 880
1792 Hydroxyacetic or Glycolic Acid 882
1793 Dehydroglycolic Acid and Glycolide 883
1794 Diglycolic Acid . . . . *ib.*
1795 Etheric Acids derived from Hydroxyacetic Acid . . . 884
1796 Thioglycolic and Thiodiglycolic Acids . . . . . *ib.*
1797 Hydroxypropionic or Lactic Acids . . . . . . *ib.*
1798 α-Hydroxypropionic, Ethylenelactic or Hydracrylic Acid . *ib.*
1799 β-Hydroxypropionic, Ethylidenelactic or Methhydroxyacetic Acid 887
1800 Inactive β-Hydroxypropionic or Lactic Acid . . . . *ib.*
1801 Etheric Acids derived from Lactic Acid 889
1802 Dehydrolactic Acid and Lactide 890
1803 Sarcolactic or Paralactic Acid 891
1804 Trichlorolactic Acid 893
1805 Chloralide and Analagous Compounds . . . . . *ib.*
1806 Hydroxybutyric Acids 895
1807 Hydroxypentylic or Valeric Acids 896
1808 Hydroxycaproic Acids . . . . *ib.*
1809 Hydroxyheptylic Acids 897

NO. OF PARAGRAPH PAGE
1810 Hydroxyoctylic Acids 898
1811 Hydroxydodecylic Acids . . . . ib.
1812 Other Hydroxy-Acids of the Acetic Series 899
1813 Dihydroxyacetic or Glyoxylic Acid . . . . . ib.
1814 αβ-Dihydroxypropionic or Glyceric Acid 902
1815 β^2-Dihydroxypropionic Acid 903
1816 Trihydroxybutyric Acid . . . . ib.
1817 Penthydroxycaproic Acids . . . . ib.
1818 Ketonic Acids of the Acetoformic Series, $C_nH_{2n-1}O.COOH$. ib.
1819 Acetoformic, Pyruvic or Pyroracemic Acid 904
1820 Hydroxyacetoformic or Carbacetoxylic Acid . . . 906
1821 Dehydro-αβ-dihydroxybutyric Acid . . . . . ib.
1822 Acetoacetic Acid . . . . ib.
1823 Preparation of Ethylic Acetoacetate 909
1824 Properties of Ethylic Acetoacetate . . . . . . ib.
1825 Metallic Derivatives of Ethylic Acetoacetate . . . 911
1826 Action of Sodium on Ethereal Acetates other than Ethylic Acetate . . . . ib.
1827 Production of Compounds of the form $CH_3.CO.CHX.COOC_2H_5$ and $CH_3.CO.CXY.COOC_2H_5$ from Ethylic Acetoacetate . 912
1828 Action of Alkalies on Ethylic Acetoacetate and its Derivatives 913
1829 Action of Nitrous Acid on Ethylic Acetoacetate and its Homologues 915
1830 Action of Sodium on the Ethylic Salts of Homologues of Acetic Acid . . . . ib.
1831 Dehydracetic Acid 916
1832 Ethylic Ethoxyacetoethoxyacetate 917
1833 Lævulinic Acid or β-Acetopropionic Acid . . . . ib.
1834 Ricinoleic Acid . . . . ib.

§ III. Acids of the $C_nH_{2n}(COOH)_2$ or Succinic Series.

1835 Acids of the Succinic Series 918
1836 Methods of Formation of Acids of the Succinic Series . . ib.
1837 Properties of Acids of the Succinic Series 920
1838 Oxalic Acid—Oxalates . . . . ib.
1839 Malonic or Methanedicarboxylic Acid 925, 1012
1840 Ethanedicarboxylic Acids 925
1841 Succinic Acid . . . . ib.
1842 Succinic Anhydride 927
1843 Thio-derivatives of Succinic Acid 928
1844 Ethylic Diacetosuccinate . . . . ib.
1845 Action of Alkali Metals on Ethylic Succinate . . . ib.
1846 Isosuccinic or Methylmalonic Acid 930

NO OF. PARAGRAPH PAGE

1847 Propanedicarboxylic Acids 930
1848 Tetranedicarboxylic Acids 932
1849 Pentanedicarboxylic Acids . . . . . . ib.
1850 Hexanedicarboxylic Acids 933
1851 Azelaic or Anchoic Acid . . . . ib.
1852 Sebacic Acid 934
1853 Brassylic Acid . . . . ib.
1854 Rocellic Acid . . . . ib.
1855 Haloid Derivatives of Acids of the Succinic Series . . ib.

§ IV. Amido- and Hydroxy-Acids derived from Acids of the Succinic Series.

1856 Amidomalonic or Glycinecarboxylic Acid 935
1857 Asparagine 936
1858 Asparaginic or Aspartic Acid . . . . . . ib.
1859 Glutaminic Acid 937
1860 Table of Hydroxy-acids derived from Acids of the Succinic Series . . . . ib.
1861 Tartronic or Hydroxymalonic Acid 938
1862 Mesoxalic or Dihydroxymalonic Acid . . . . . ib.
1863 Malic or Hydroxysuccinic Acid 939, 1012
1864 Isomalic or Hydroxyisosuccinic Acid 941
1865 Tartaric or Dihydroxysuccinic Acid . . . . . ib.
1866 Dextrotartaric Acid . . . . ib.
1867 Lævotartaric Acid 943
1868 Racemic Acid 946
1869 Mesotartaric Acid 948
1870 Hydroxypropane-α-dicarboxylic Acids—Glutanic Acid . 949
1871 Hydroxypyrotartaric Acids—Itamalic Acid—Citramalic Acid ib.
1872 Aposorbic Acid . . . . ib.
1873 Hydroxyadipic Acids . . . . ib.
1874 Dimethyltartaric Acid . . . . ib.
1875 Diaterebic Acid 950, 1012
1876 Diaterpenylic Acid 950
1877 Saccharic Acid . . . . ib.
1878 Mucic Acid 951

§ V. Tribasic Acids derived from the Paraffins.

1879 Tricarballylic Acid 952
1880 Citric Acid . . . . ib.
1881 Hydroxycitric Acid 953
1882 Desoxalic Acid 953, 1012

NO. OF PARAGRAPH PAGE

§ VI. Acids of the Acrylic Series.

1883 Table of Acids of the Acrylic Series 953
1884 Methods of Formation of Acids of the Acrylic Series . . 954
1885 Properties of Acids of the Acrylic Series . . . . *ib.*
1886 Acrylic Acid 955
1887 Crotonic Acid—Isocrotonic Acid—Methacrylic Acid . . 957
1888 Dimethacrylic Acid—Tiglic Acid—Angelic Acid . . 958
1889 Hydrosorbic Acid—Pyroterebic Acid—Ethylcrotonic Acid . 961
1890 Higher Acids of the Acrylic Series—Teracrylic Acid—Damaluric Acid—Moringic Acid—Cimicic Acid—Hypogæic Acid—Oleic Acid—Erucic Acid 962
1891 Haloid Derivatives of Acids of the Acrylic Series . .
1892 Chloracrylic Acids 965
1893 Bromacrylic Acids . . . . *ib.*
1894 Haloid Derivatives of Acids of the Formula $C_3H_5.COOH$. 966

§ VII. Acids of the Maleic Series.

1895 Table of Acids of the Maleic Series 967
1896 Fumaric Acid . . . . *ib.*
1897 Maleic Acid 968
1898 Pyrocitric Acids 969
1899 Crotaconic Acid 971
1900 Haloid and Hydroxy-Derivatives of Maleic, Fumaric, 'and Pyrocitric Acids . . . . *ib.*
1901 Hydromuconic Acid 973
1902 Aconic Acid—Paraconic Acid—Muconic Acid . . . *ib.*
1903 Xeronic Acid 974
1904 Camphoric Acids . . . . *ib.*
1905 Camphoric Anhydride 976
1906 Acids formed together with Camphoric Acid by the Oxidation of Camphor 977
1907 Constitution of Camphoric Acid 979

§ VIII. Acids of the Aconitic Series.

1908 Aconitic Acid—Diconic Acid 980

§ IX. Acids of the $C_nH_{2n-3}.COOH$ Series.

1909 Table of Acids of the Sorbic Series . . . . . *ib.*
1910 Tetrolic Acid . . . . *ib.*
1911 Sorbic Acid 981
1912 Diallylacetic Acid . . . . *ib.*
1913 Palmitolic Acid . . . . *ib.*
1914 Stearolic Acid 982
1915 Behenolic Acid . . . . *ib.*
1916 Tetrahydrobenzoic or Benzoleic Acid . . . . . *ib.*

NO. OF PARAGRAPH PAGE

§ X. Acids of the $C_nH_{2n-4}(COOH)_2$ Series.

1918 Acetylenedicarboxylic Acid 983

§ XI. The Van't Hoff-Le Bel Hypothesis of Isomerism.

1919 Insufficiency of the present Theory of Isomerism . . *ib.*
1920 The Van't Hoff-Le Bel Asymmetric Carbon Atom Hypothesis 986
1921 Constitution of Optically Active Bodies 989
1922 Probable Insufficiency of the Van't Hoff-Le Bel Hypothesis 991

§ XII. Acids of the Furfuryl Group.

1923 Pyromucic Acid 993
1024 Isopyromucic Acid—β-Pyromucic Acid 996
1925 Furfuracrylic Acid . . . . *ib.*
1926 Furfurangelic Acid . . . . *ib.*
1927 Constitution of the Furfuryl Compounds . . . . *ib.*
1928 Dehydromucic Acid 997
1929 Meconic Acid 998
1930 Comenic Acid . . . . *ib.*
1931 Pyromeconic Acid 999

Additions, Corrections, and Cross References . 1000—1012

PART III.

CHEMISTRY OF THE CARBON COMPOUNDS;

OR

ORGANIC CHEMISTRY.

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CHAPTER I.

§ I. *Introductory;*—§ II. *Analysis of Carbon Compounds;*—§ III. *Molecular Formulæ.*

(1025) Organic Chemistry, in its primary signification, treated of the chemistry of organized beings, and of the products of their chemical actions upon matter in its various forms, it being supposed until the year 1828 that the interposition of the so-called vital force was essential to their formation. At that time, however, the celebrated German chemist, Wöhler, showed that *urea*, which occurs in the urine of man and animals, could be artificially prepared. Since then a number of carbon compounds have been produced which had previously been known only as derived from animal or vegetable substances; amongst others, well known substances such as alcohol, tartaric acid, glycerin, and indigo, also alizarin—the colouring matter of madder, gallic acid—found in gall nuts, and coumarin the odoriferous principle of the Tonka bean. There is but little doubt, as new methods are discovered, and our knowledge of the carbon compounds increases, that we may eventually be able to produce synthetically even the most complex.

Organic chemistry, therefore, in its present signification is *the chemistry of carbon compounds*; the chemistry of the remaining elements, and the compounds they form with one another, constituting the so-called inorganic chemistry. It is important therefore to bear in mind the distinction between *organic compounds* and *organized bodies*.

Organic compounds possess a *definite composition*, and in many cases exhibit a crystalline structure, such as may be observed in sugar, oxalic acid, urea, taurin, and quinine.

On the other hand, *organized bodies*, such as muscular tissue, nerve structure, cellulin, and ligneous fibre, never exhibit any tendency to a crystalline arrangement, but show a rounded, vesicular, or fibrous configuration; and are so connected with each other as to form parts of a system, each of which is incomplete if severed from the remainder. Their composition, however, *is not invariable*, and there can be no doubt that they are mixtures of several compounds, and consequently not perfectly homogeneous. It should be remembered that the power of the chemist is confined to the preparation of definite chemical compounds and the investigation of their properties, for organized bodies have not hitherto been prepared artificially: they are the result of the action of living bodies upon inanimate matter, every living body having the power of assimilating fresh matter from without, and of arranging its particles in the special form which characterizes the class to which the individual organism belongs.

The study of the chemical changes that occur in living bodies constitutes *physiological chemistry*, one of the most difficult and least investigated branches of the science. The difficulty depends, in a great measure, on the extreme delicacy of the arrangements by which the various changes are effected, and upon their complicated nature which renders them liable to injury from a multiplicity of causes that have hitherto eluded scrutiny. Important changes may in consequence often be effected in the organism itself without being appreciable except in their results, even when they extend so far as to occasion death. We can proceed to investigate the effect produced by the tying of a large artery or the division of a nerve; but when an animal is poisoned by a few milligrammes of aconitine or by a few drops of a solution of hydrocyanic acid, there is scarcely anything to indicate to the anatomist, to the microscopic observer, or to the chemist, the mode in which these bodies operate in suddenly cutting short the life of the animal. The organization still appears to be perfect, yet the once living mechanism no longer continues to perform its wonted functions. In the living body compounds are produced, many of which, when released from the influences under which they originated, quickly undergo fresh changes; these are generally manifested by the occurrence of the putrefaction and decay to which both animal and vegetable tissues are liable when they no longer form a part of the living organism. A continuous renewal of their constituents is one of the distinguishing and essential characteristics of living bodies, so that when the plant or the animal is performing its functions in a healthy manner, a series of changes succeed each other in a regular order; but if this sequence be modified, even in a slight degree, disease frequently ensues, and when the change is extensive, death is the speedy and inevitable consequence.

The attention devoted to physiological chemistry of late years has led to most important results, and there is no doubt that more extended investigation will enable us to ascertain the nature of many of the chemical phenomena to which animal and plant life give rise. In the present work the attention of the reader will be only incidentally directed to the physiological portion of the subject, the main object being to exhibit the mutual relations which the various chemical compounds bear to each other, and to trace the laws of their formation.

§ II. ANALYSIS OF CARBON COMPOUNDS.

(1026) The greater number of organic compounds are composed of a small number of elements, yet they present properties as much opposed to each other as it is possible to imagine: some of these products constitute the daily food of man, others act as direct and violent poisons.

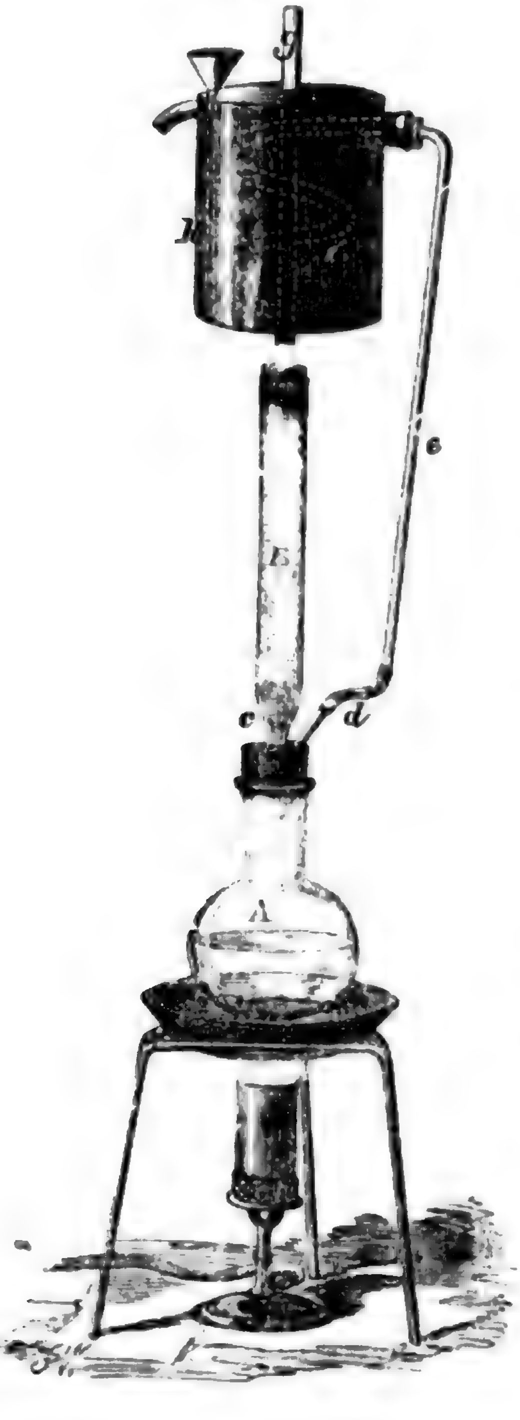
A large and very important class of carbon compounds, including many essential oils and such substances as naphthalene, benzene, and paraffin, consist of carbon and hydrogen only; the greater number of organic bodies, however, derived from the vegetable kingdom, contain carbon, hydrogen, and oxygen, like sugar, acetic acid, and alcohol; others contain nitrogen in addition to these elements, and in some few sulphur occurs. The majority of the organic compounds obtained from the animal kingdom consist of carbon, hydrogen, oxygen, and nitrogen, whilst a few also contain sulphur and phosphorus. Organic compounds have been artificially prepared containing not only the elements just enumerated, but chlorine, bromine, iodine, fluorine, silicon, boron, and the metals.

Although the number of different elements associated with carbon in organic substances is usually small, they may possess any degree of complexity from hydrocyanic acid, HCN, containing only three atoms in the molecule, to the complex substance stearin, $C_{57}H_{110}O_6$, with its 173 atoms, or the still more complex compound albumin, the molecule of which ($C_{72}H_{112}N_{18}SO_{22}$) contains not less than 225 atoms, and perhaps even more.

(1027) **PROXIMATE ANALYSIS.**—It is necessary in the examination of any organic substance to ascertain its composition, or in other words, to analyse it. As, however, it may happen that it is not a definite compound, but a mixture of two or more, the problem then presented to the chemist is to separate the proximate components from each other. The analysis of organic substances may therefore be conveniently considered under *proximate analysis,* as in the separation of wheat flour into starch, sugar, gluten, ligneous fibre, and oily matter; and *ultimate analysis,* or the determination of the proportions in which the carbon, hydrogen, and oxygen are united in the starch, sugar, or gluten.

The proximate analysis of an organic substance is often a matter of considerable difficulty, so that no general rule can be laid down for the separation or extraction of the different principles, each class of substances requiring special treatment, which experience alone can indicate.

FIG. 377.



In all cases of proximate analysis, the employment of the microscope will afford valuable aid whilst watching the progress of the separation, and in enabling the operator to ascertain whether or not the substances which he has isolated are mixed with other bodies. When the substance is crystalline, such an examination, by showing whether one or more forms of crystal are present, is often more valuable for ascertaining the purity of the body than the use of chemical reagents.

(1028) *Separation by Solvents.*—The process generally followed in the first instance is to subject the dry pulverised material to the action of several solvents in succession, such as ether, alcohol, and water.

A convenient apparatus for the digestion of the substances for analysis in these menstrua, is shown in fig. 377:—A is a glass flask containing the liquid solvent, which can be kept in steady ebullition by means of the lamp beneath. B is a tube of glass or of tin-plate, in the contracted portion of which is a plug of cotton wool, *c*; in this tube the substance is to be placed; *d*, is a short lateral tube to which the tube, *e*, of glass or metal, is attached by india-rubber tubing. The tube *e* should be kept warm by enveloping it in flannel, with a view to prevent the premature condensation of the vapour as it rises from the flask. M is a tin-plate condenser, which can be filled with water; *h* is a funnel for conveying cold water to the bottom of this vessel, whilst the hot water flows off at the spout above. A tube, *g*, open at both ends, passes through the axis of M; the lower projecting extremity of this tube is fitted by a cork to the tube B. *f* is a worm tube, the upper extremity of which passes through the side of the refrigerator, and is adapted by a cork to the tube *e*, whilst its lower extremity is soldered to the tube *g*, into which its contents flow after they have been condensed in their passage through the refrigerator. It is obvious that by this arrangement a perpetual distillation of the liquid in the flask A may be readily maintained; the vapour which passes through the tube *e* becomes condensed in the spiral tube *f*, and percolates, in the liquid form, through the material contained in B, carrying the soluble matters into the flask A, where they gradually accumulate. If the employment of metal be in any case objectionable, glass vessels may be used.

A great variety of solvents are now employed for the separation and purification of carbon compounds, so that a slight sketch of their most salient properties may be useful. *Ether* is especially valuable from its low boiling point, and from its having no chemical action on most organic compounds; so that on distilling off the ether the dissolved substance is easily recovered without having undergone any sensible decomposition. In addition to this, it has the advantage of dissolving a very large number of substances which are comparatively insoluble in other liquids. *Alcohol* is also largely used, and may be advantageously employed for dissolving such substances as the alkaloids; but, as a rule, it should be avoided, if possible, for halogen substitution compounds, as it is very liable to react with them, and cause their decomposition, or at least partially. *Water* dissolves sugar, gum, starch, and other highly oxidized bodies which are nearly insoluble in ether or alcohol, also many salts, both of organic acids and bases. *Benzene* is a very useful solvent, especially for chlorine, bromine, and iodine substitution compounds, but for this purpose it should be purified by digestion with concentrated sulphuric acid. This removes certain hydrocarbons which usually accompany it in coal oil, and which would otherwise decompose the dissolved substance. A peculiar characteristic of benzene in which it differs greatly from alcohol and ether is that almost all amorphous substances are insoluble in it. The homologues of benzene found in coal oil, such as toluene, xylene, &c., are also occasionally useful when a solvent of a somewhat higher boiling point is required. Organic compounds generally are much less soluble in *carbonic bisulphide, carbonic tetrachloride* and *chloroform* than in benzene, and consequently their use is somewhat restricted. Glacial *acetic acid* possesses valuable solvent properties, and the fact that it dissolves chromic anhydride and nitric acid, whilst it is not attacked by them, renders it exceedingly useful in moderating their action on carbon compounds. Light *petroleum* oil, consisting principally of the lower boiling-point paraffins, is also useful, usually for the crystallization of substances which are exceedingly soluble in ether, benzene, and carbonic bisulphide; its solvent powers are not great. *Nitrobenzene, aniline,* and *oil of turpentine* are also occasionally used. In particular cases *dilute acids,* and in others *dilute alkalies* may be employed, but they must be used with caution, as they are liable to act not merely as solvents, but also to produce chemical changes in the compounds submitted to their action.

(1029) *Fractional Crystallization and Fractional Solution.*—It frequently happens that two or more crystalline substances occur together, which possess different degrees of solubility in the same menstruum; in such a case they may often be separated by *fractional crystallization,* care being taken to collect the crystals as soon as a portion of the compound has been deposited, and keeping them separate from those which are formed subsequently; by repeating this process on the first portions, the less soluble compound may be obtained in a state of purity.

In some cases, where a mixture of two solids of very unequal solubility in the same menstruum is operated on, *fractional solution* may be employed. In this case, by using successive small portions of the sol.ent, the more soluble ingredient may be gradually removed, leaving undissolved the less soluble ingredient in a nearly pure state.

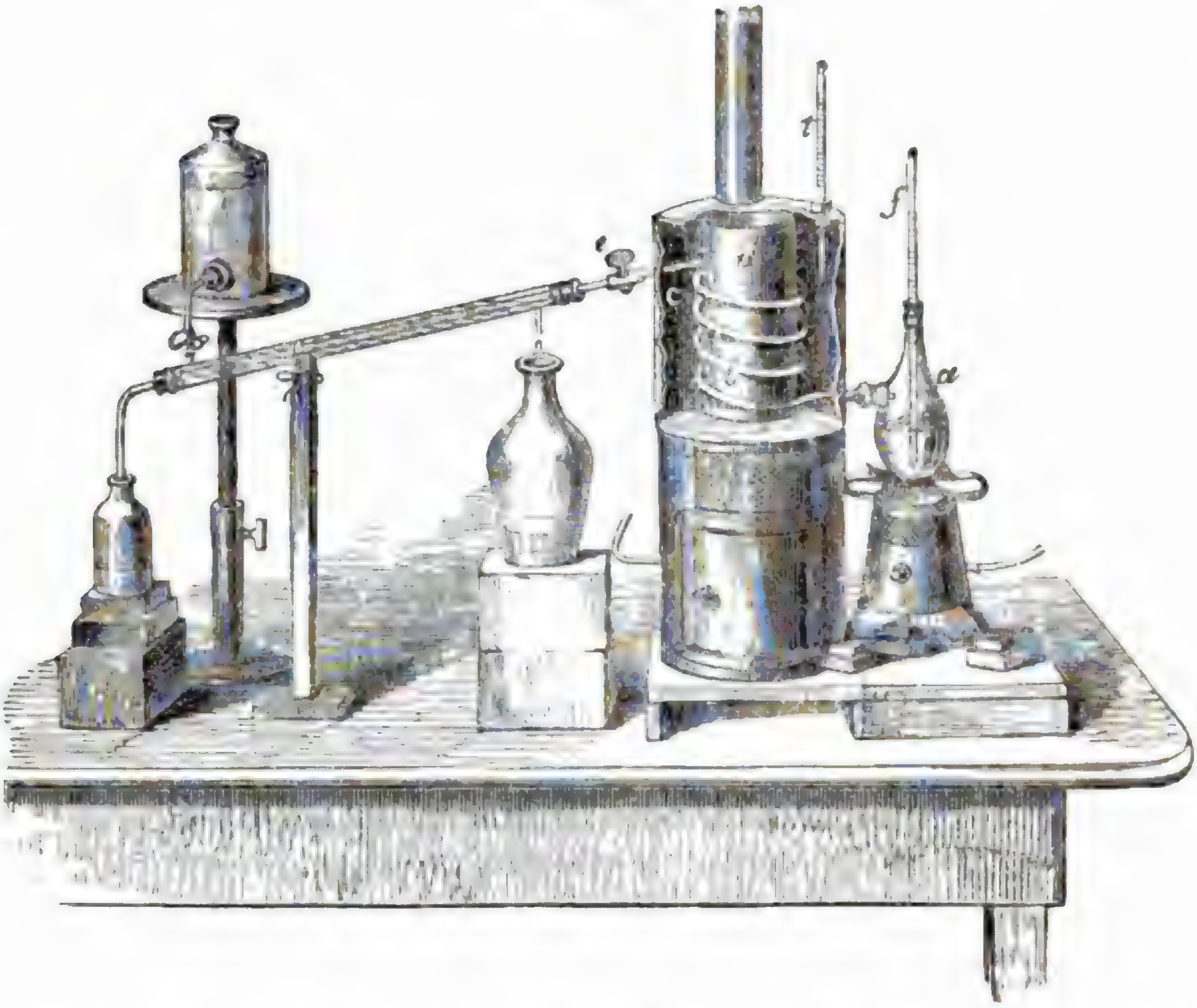
(1030) *Fractional Precipitation and Fractional Saturation.*—In other cases, if the different compounds yield precipitates with the same reagent, a separation by *fractional precipitation* may be effected by adding a quantity of the precipitant insufficient to throw down, for example, more than one-half of the amount of the substances that may be present. The salts of silver or of lead may thus be employed for separating certain organic acids, particularly the fatty or the resinous acids, or others which like them greatly resemble each other in properties. The precipitate must then be suspended in water, and decomposed by means of sulphuretted hydrogen, or of a dilute mineral acid, in order to separate the metal and liberate the organic acid, which is again submitted to a similar partial precipitation. This process must be repeated until the fusing point becomes constant, or some other guarantee of the purity of the body is obtained.

A method, which may be termed *fractional saturation*, was applied by Liebig to the separation of certain volatile acids from each other. This process consists in partially saturating the acid with potassic or sodic hydrate, and then distilling; the more volatile acid passing over with the distillate. Suppose that it be desired to effect the separation of butyric from valeric acid by this means:—a certain amount of potassic hydrate is added, and if this be more than sufficient to saturate the valeric acid, the distillate will consist of butyric acid only, while the residue will be a mixture of potassic valerate and butyrate. If, on the other hand, the potassic hydrate be insufficient to completely saturate the valeric acid, the residue in the retort will consist of pure potassic valerate, and the distillate will be a mixture of butyric and valeric acids, which may be separated by a repetition of the process.

(1031) *Fractional Distillation.*—The operation of *fractional distillation* is employed for the separation of mixed volatile liquids whose boiling points differ to some extent. The mixed liquid to be operated on is placed in a retort, into the tubulure of which a thermometer is inserted, and heat is applied until the liquid boils. The bulb of the thermometer, however, should not dip into the boiling liquid, for its temperature is usually far higher than that of the vapourized portion, and, consequently, an incorrect boiling point would probably be assigned to the distillate. In distilling such a mixture, it will generally be found that although the temperature of the vapour, as indicated by the thermometer, rises continuously, yet at certain points this takes place much more slowly, the temperature, for a time, remaining nearly stationary. A large quantity of the liquid will then distil within comparatively small limits of temperature, and may be supposed to have a composition nearly uniform. By again rectifying those portions which distil within the same small limits of temperature, the different components of the mixed liquid may be obtained in a state of tolerable purity. Where large quantities can be operated on, this process may be employed for the separation of liquids the boiling points of which differ considerably from each other; but it is not satisfactory when the quantities are small, or where the boiling points are within 10° or 15° (20° or 30° F.), of each other. Except with liquids of high boiling point, it is generally better to substitute for the retort a flask furnished with a bent tube connected with a condenser, and a thermometer, the bulb of which should be about half way down the neck of the flask.

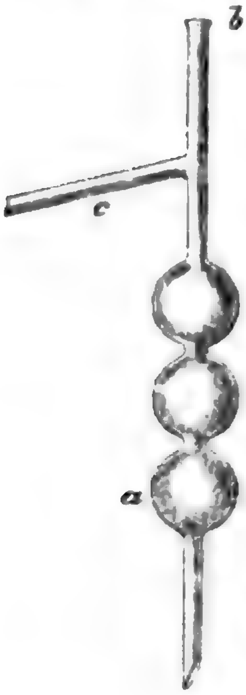
A considerable improvement in the mode of conducting the fractional distillation of comparatively large quantities of liquid was introduced by Warren, who applied it successfully in examining the volatile products of American petroleum. (*Memoirs of the American Academy*, New Series, vol. ix.) This mode of distillation will be understood from an examination of fig. 378, in which *a* shows the retort or two-necked flask containing the liquid for distillation together with a thermometer *f*. The flask is connected with an ascending spiral worm *b*, which is maintained at a constant temperature by being made to pass through the oil bath *c*, heated from below, and having the temperature regulated by the aid of the thermometer, *t*. *d* is a vessel ordinarily empty, but which can be filled with ice if it is required to keep the worm at a low temperature. The upper end *e* of the worm is connected with a Liebig's condenser or other suitable apparatus for condensation. By this arrangement it is easy to ensure the condensation of the less volatile portions, which flow back into the retort, whilst the more volatile portion passes on and is condensed in the colder part of the apparatus. The apparatus should be made of brazed copper; the worm is about 5 feet, or 1·5 metre in length, and $\frac{3}{8}$ inch or 10 millimetres in internal diameter.

Fig. 378.



The piece of apparatus represented in fig. 379 acts much in the same way as Warren's, and is very generally used in the laboratory for facilitating the fractional distillation of liquids. It consists of a tube about half an inch (13 millimetres) in internal diameter, on which are blown from three to six bulbs, the lowest one, *a*, being about six inches (15 centimetres) from the cork; a thermometer is inserted into the upper end *b*, the bulb of which comes just below the exit tube *c*, for the vapour. This is connected with a suitable condensing arrangement for the collection of the distilled liquid. Here the large surface exposed by the bulbs has an effect similar to the worm of Warren's apparatus in condensing the less volatile portion of the vapour. The distillation should be conducted very slowly and in a place as much sheltered from currents of air as possible.

FIG. 379.



Linnemann (*Ann. Chem. Pharm.* clx. 195), has considerably improved on this apparatus by the introduction into the distilling tube of small cups (fig. 380), made of fine platinum wire gauze, the meshes of which are about 0·75 millimetres square, or 35 to the inch. For the separation of liquids whose boiling point is below 150° (302° F.), it is advisable to use at least eight such cups; those boiling between 150° and 180° (302° and 356° F.) require six cups, whilst above 180° (356° F.) five are sufficient. These cups (fig. 381) are made by pressure in a box-wood mould and slide with friction in a tube which should be from 9 to 12 millimetres ($\frac{3}{8}$ to $\frac{1}{2}$ inch) in internal diameter. During the progress of the distillation these become partially filled with the liquid which condenses on the sides of the tube, so that the vapour is compelled to pass through the liquid and becomes washed as it were, only the more volatile portion passing on to the condenser; its action is therefore almost identical with the Coffey's still, used for the rectification of alcohol on the large scale. After a time the platinum cups will become too full; the burner must then be removed for a few seconds from under the distilling flask, so as to stop the boiling and allow the liquid to flow back again into the flask, after which the distillation can be resumed.

FIG. 380.

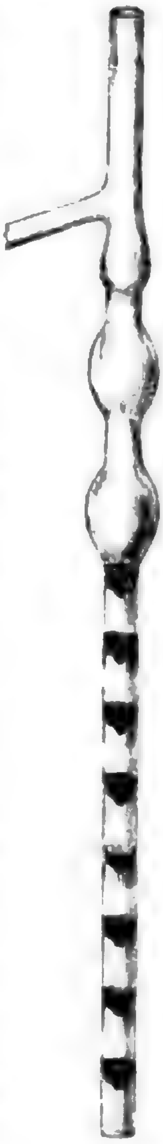
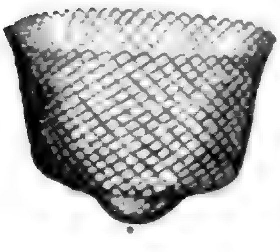


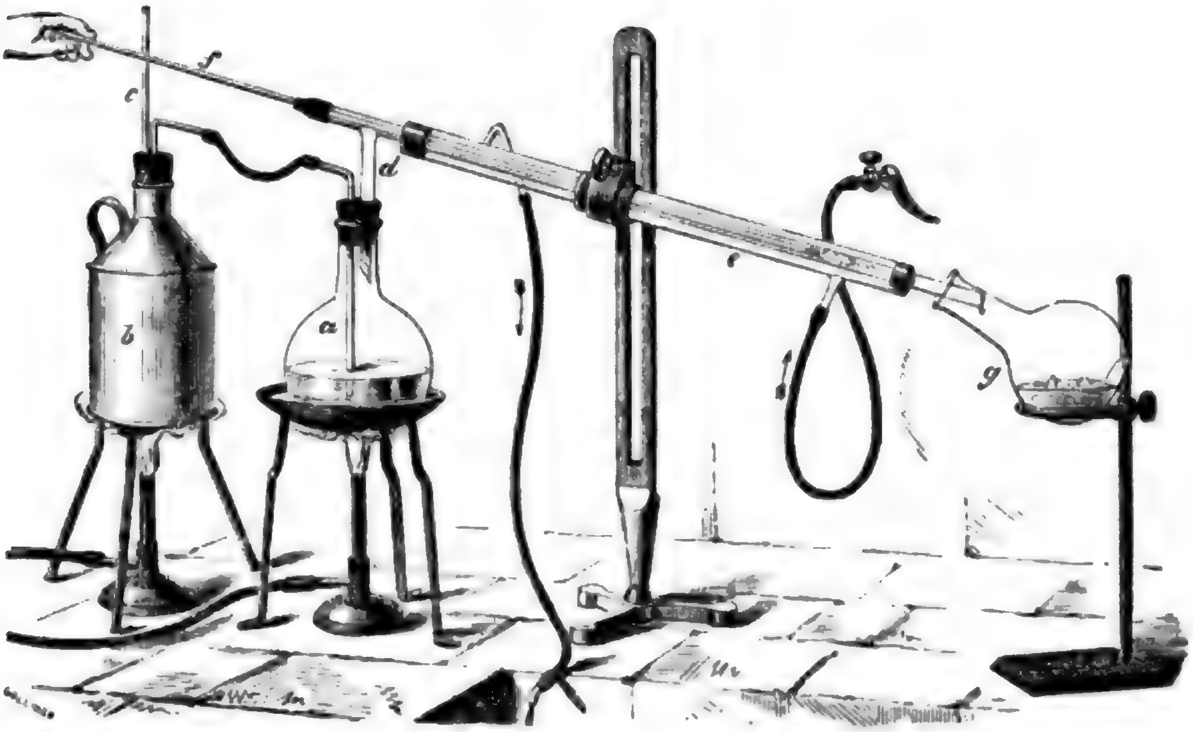
FIG. 381.



Wanklyn has shown (*Proc. Roy. Soc.*, xii. 534) that the proportions in which mixed liquids distil over must vary not only with the relative amount of each constituent, and with the tension of the vapour of each at the boiling point of the mixture, but also with the adhesion of the liquids to each other and with the vapour density of each. Although in most cases the effect of adhesion is trifling, the variation in vapour density is important. According to his experiments, a mixture of equal weights of two liquids of different boiling points will furnish a distillate in which the proportion of each liquid may be calculated from the product of the tension into the specific gravity of the vapour. In consequence of this circumstance, the less volatile liquid may distil over more rapidly than the other; for example, a mixture containing 18 parts of wood spirit (boiling at 66° (151° F.), vapour density 15·5), and 17 parts of ethyl iodide (boiling at 72° (161°·6 F.), vapour density 78) yielded in the first third a mixture consisting of 6 parts of wood spirit and 8·7 of ethyl iodide. If the vapour density and the tension at the boiling point of the mixed liquids are inversely proportional in the case of the two liquids, the mixture distils without change. These observations explain the facility with which bodies of high boiling point and of considerable vapour density, such as the essential oils, pass over with the vapour of water. Berthelot has made similar observations.

It frequently happens that a mixture of substances is obtained, one or more of which are readily volatile in a current of aqueous vapour, thus affording an excellent method for separating them from those which are non-volatile under these circumstances. The mixture is introduced into a flask *a*, fig. 382, contain-

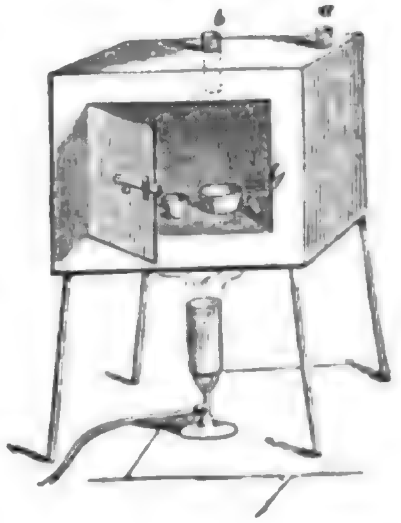
Fig. 382.



ing water which is kept gently boiling, whilst a current of steam from a tin or copper can, *b*, is passed into the liquid by means of a tube reaching nearly to the bottom of the flask. The aqueous vapour and the volatile substances pass out through the tube *d*, and after being condensed in *e*, are received in the flask *g*, whilst the non-volatile portion remains in the flask *a*. When solid substances are operated upon, the long glass rod *f*, which is fitted to the condenser by means of a short piece of caoutchouc tube, serves to clear out any obstruction which might be caused by the condensation of the solid in the tube *e*. The safety tube *c* reaches to within about an inch of the bottom of the tin can *b*.

(1032) Ultimate Analysis.—Scrupulous attention to the purity of the matter submitted to analysis is of course of primary importance, a very slight admixture with other compounds being sufficient to vitiate the conclusions deducible from the experiments. Having by suitable means ascertained the purity of the substance to be analysed, the next care is to insure its complete desiccation. Solids should be finely powdered and dried in the hot water oven, if they are not decomposed at 100° (212° F.); otherwise they must be dried in vacuo at the ordinary temperature over sulphuric acid. Volatile liquids that are unchanged by distillation should be allowed to stand for two or three days upon fragments of fused calcic chloride; the liquid should then be decanted and distilled in a small retort. In the examination of fats or fixed oils, it is more convenient to dry the material in a watch-glass placed in an ordinary water-bath, or by exposing them to a temperature of from 100° (212° F.) to 120° (248° F.) in a *water oven* or box of sheet copper, made double, as shown in fig. 383; *a* being an aperture for the introduction of water or of oil into the space between the external and internal plates, the heat being supplied by a gas flame below, and the temperature being regulated by a thermometer introduced into the liquid through the opening at *a*. By weighing the substance before and after drying, the loss which it experiences can be accurately ascertained.

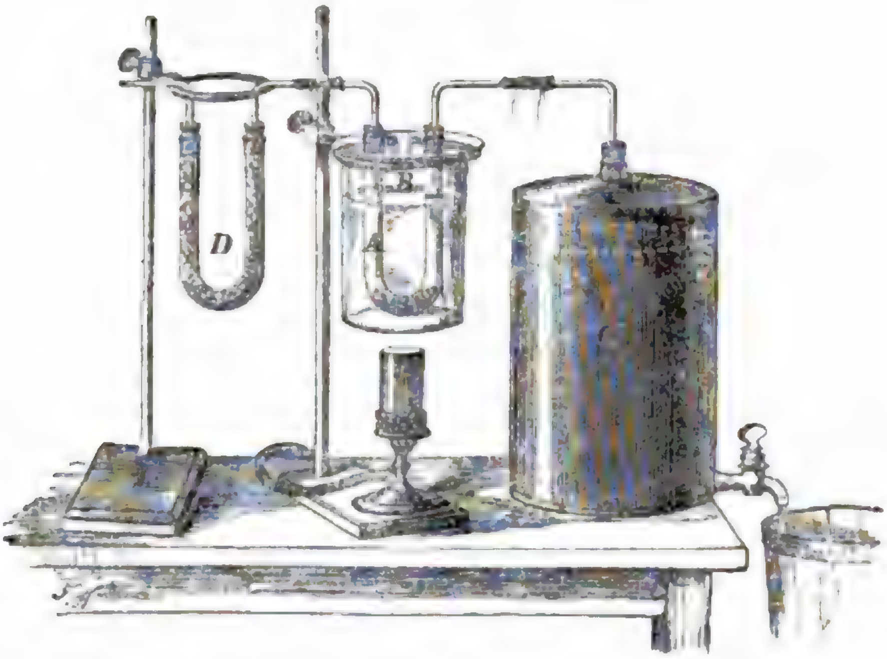
Fig. 383.



If the substance is very hygroscopic the apparatus shown in fig. 384 may be employed. A represents a bent glass tube, for the reception of the substance to be dried; B is a vessel of glass or of metal, containing water or oil, or some saline solution; C, an aspirator, by which a current of atmospheric air can be maintained through the apparatus; and D, a bent tube filled with fragments of pumice-stone, soaked in sulphuric acid, for drying the air as it enters. The tube A with its contents is weighed at the beginning of the operation, and the desiccation must be continued until it ceases to lose weight.

If the desiccation be effected in the water oven, the ground watch glasses which contain the compound should be allowed to cool under a bell glass, over a dish of sulphuric acid or calcic chloride.

Fig. 384.



(1033) *Determination of Carbon, Hydrogen and Nitrogen.*—Most organic compounds consist of carbon, hydrogen, oxygen, and sometimes nitrogen, so that the operation of organic analysis resolves itself mainly into the accurate quantitative determination of these elements. We are indebted to Gay-Lussac and Thénard for the fundamental principle that regulates our operations in this respect, although the process proposed by them has subsequently been modified and improved by many chemists, especially by Berzelius, De Saussure, Prout, and Liebig. It was by the last named eminent philosopher that the method now in general use was contrived.

The object of the operation being to determine the relative proportion in which each of the elements occurs in the compound under examination, it is necessary for the success of the analytical process that these elements should either be separated in a state of purity, or obtained in the form of definite compounds that can easily be collected. In practice it has been found most convenient to supply the substance to be analysed with a quantity of oxygen sufficient to convert the carbon which it contains into carbonic anhydride, and the hydrogen into water. An arrangement is made for estimating the water, by causing the evolved gases to pass over a substance which has a powerful attraction for it, such as calcic chloride or pumice moistened with sulphuric acid, whilst the carbonic anhydride is absorbed by means of a solution of potassic hydrate; when the amount of nitrogen has to be ascertained it is either measured over mercury in the form of gas, or determined as ammonia. In the latter case, the substance to be analysed is mixed with soda-lime, and heated; all the nitrogen is thus converted into ammonia, in which form it admits of being readily estimated.

The amount of carbonic anhydride, water, and ammonia being known, it is easy to find by calculation the weight of the carbon, hydrogen, and nitrogen respectively contained in them. The quantity of oxygen which the substance contains may be known by deducting the united weight of the carbon, hydrogen, and nitrogen, from the total weight of the body analysed, supposing no other elements to have been present.

The method employed for the analysis will vary according to the nature and composition of the substance to be examined.

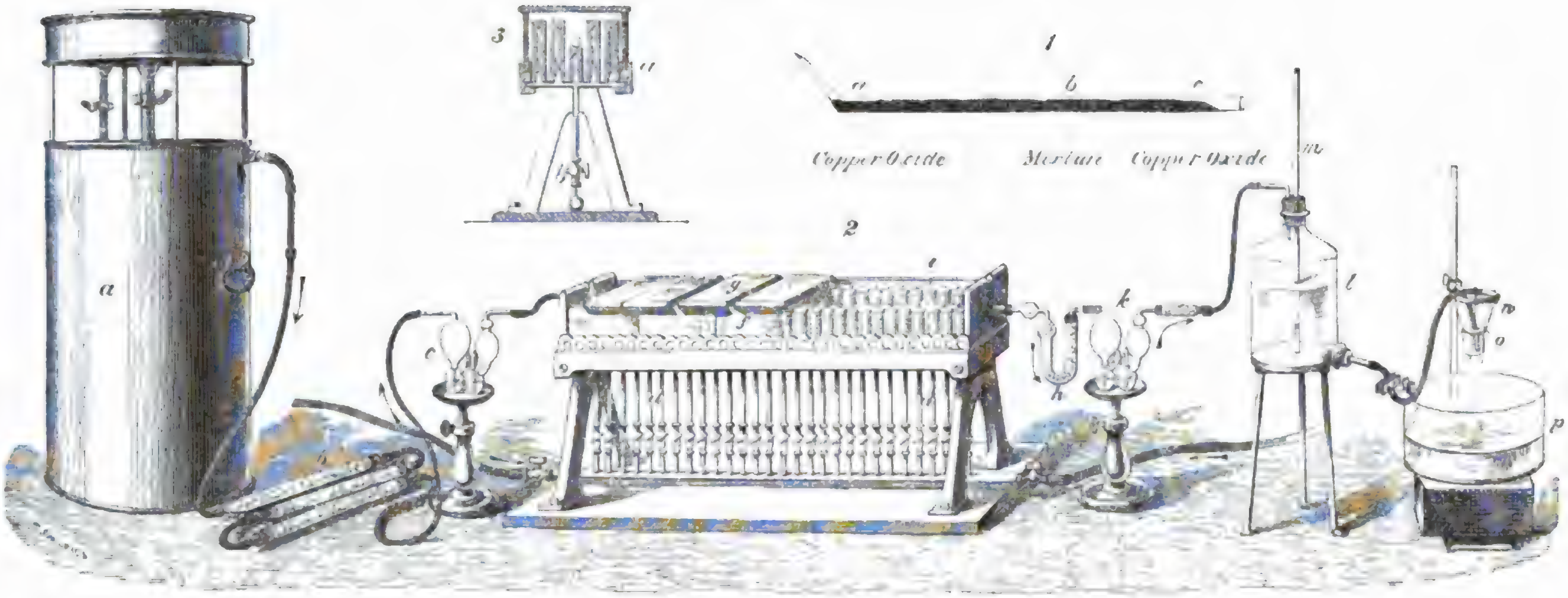
We shall first describe the methods of analysing—

1. A *solid*, which does not contain nitrogen.
2. A *liquid*, which does not contain nitrogen.
3. A substance which does contain nitrogen.

(1034) *Analysis of a Solid not containing Nitrogen.*—As gas is now so readily obtainable it is almost universally used in the furnaces employed for organic analysis. Many forms of gas furnace for this purpose have been devised, differing considerably in detail, but that originally proposed by Hofmann is perhaps the most generally useful in an ordinary laboratory. Its general arrangement is represented at 2, fig. 385. A firm cast iron stand supports the body of the furnace shown in section at 3. The gas issues through a number of minute holes in the fire clay burners of which there are five rows, those in the centre row on which the combustion tube rests being shorter than the others; the amount of gas supplied to the fire-clay burners through the tubes *d d*, can be easily regulated by means of the stopcocks. The sides of the furnace are formed of tiles, *f*, some of which are removed to show the arrangement of the burners; other tiles *g*, which are moveable, can be placed at pleasure on the top of the furnace to assist in regulating the temperature.

Charcoal is occasionally used where gas cannot be obtained: the best form of furnace for this is represented at *c*, fig. 386: it is made of stout sheet-iron bent into the form of a trough, open at one end; the plate which closes the other end is perforated with an aperture three-quarters of an inch in diameter, to allow the passage of the combustion tube; the furnace is about 20 inches long, 5 inches wide at top, $2\frac{3}{4}$ inches at bottom, and 3 inches high; or about

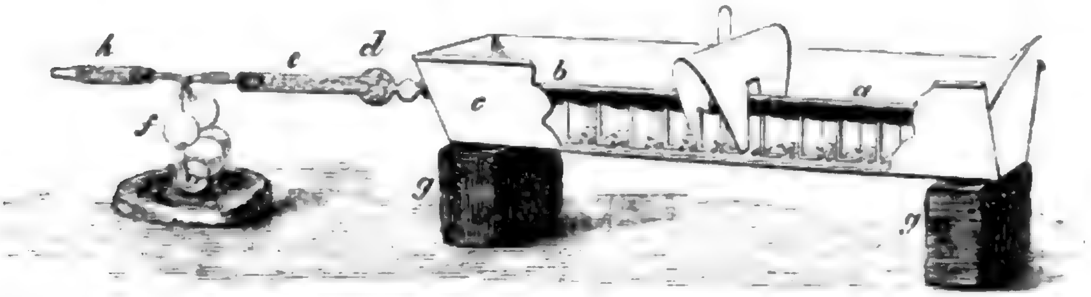
Fig. 385.


3
a
1
a
b
c
Copper Oxide
Mixture
Copper Oxide
m
2
a
e
g
f
i
d
d
h
k
l
n
o
p

Google

50 centimetres long, 13 cm. wide at top, 7 cm. at bottom, and 8 cm. high. Transverse slits are made at intervals of 2 inches along the bottom of the trough for the admission of air, and in each of the spaces between these slits is riveted a vertical stiff piece of sheet-iron, 1 inch high, terminating in a concave edge above, for the support of the combustion tube. During the operation, the furnace may rest on bricks, *g*, *g*.

FIG. 386.



The *combustion or retort tube a b*, fig. 386, in which the mixture is burned, is about 24 inches long and $\frac{3}{8}$ of an inch in diameter (60 centimetres long and 9 millimetres in diameter); it is made of glass of difficult fusibility and free from lead, such as the hard Bohemian glass. The tube is generally drawn out into a fine but strong tail bent upwards at an obtuse angle, and the mouth should be smoothed by fusing it in the flame of the blowpipe, so that the cork may not be torn in adjusting it.

The water is collected in a tube, *e*, filled with calcic chloride. At *d* is a small bulb, in which the greater part of the water becomes condensed, and may be emptied out as soon as the tube has been weighed; if this is done the calcium chloride will last for a large number of operations without requiring to be renewed. The calcic chloride must not be fused, but should be prepared by evaporating the solution of the chloride to dryness by a strong sand heat; a porous mass is thus obtained, which absorbs the aqueous vapours more readily, and at the same time does not expand like the fused variety to the destruction of the tube that contains it. The cork through which passes the short tube by which the drying tube *e* is connected with the potash bulbs *f*, and which may consist of a short piece of caoutchouc tubing, should be trimmed close to the large tube and covered neatly with melted sealing-wax; and lastly, air should be drawn through the apparatus to ascertain that no obstruction exists. Pumice-stone moistened with concentrated sulphuric acid may sometimes be advantageously substituted for calcic chloride in the drying tube. The connexion between this tube and the combustion tube, *a b*, is effected by means of a sound elastic cork, or a plug of vulcanized caoutchouc, which is made to close the mouth of the tube accurately; it is pierced with a round file, and fitted firmly upon the fine tube proceeding from the bulb *d* of the drying tube; the cork should be dried on the sand-bath immediately before the apparatus is mounted.

The solution of potassic hydrate employed in the potash bulbs, *f*, should have a sp. gr. of from 1·25 to 1·27, and must be renewed every two or three experiments. To the free end of the potash bulbs, a tube *h*, filled with fragments of potassic hydrate, is adjusted by means of a cork; this is weighed with the bulbs, and is employed to dry the nitrogen and other gases which escape during the course of the analysis. A far better form than the ordinary Liebig's bulbs are those devised by Geissler and represented at *k*, fig. 385, where the gas passes successively through three distinct bulbs, each of which contains a solution of potassic hydrate; the arrangement can be easily understood from an inspection of the figure.

The compound generally used for supplying oxygen to the substance to be burned is cupric oxide, which, although it is not decomposed when heated alone, yet readily imparts oxygen to the carbon compound heated in contact with it. It is conveniently prepared by dissolving copper in pure nitric acid, evaporating to dryness, and decomposing the nitrate by heating it in an earthen crucible until red fumes cease to appear. It should be strongly heated, otherwise it is very hygroscopic, but care must be taken that the temperature is not so high as to cause incipient fusion; in this case it becomes agglutinated, and requires pounding in an iron mortar to pulverize it. The powdered oxide should be sifted through a fine copper gauze sieve, and preserved in stoppered glass bottles. Sometimes it is convenient to use the granular semifused cupric oxide produced by strongly heating copper in a current of air in a muffle.

Immediately before each analytical operation, a sufficient quantity of cupric oxide is to be ignited in a crucible, and while still very hot, transferred to a dry tube, by plunging the mouth of the tube into the oxide in the crucible, and then by a turn of the wrist causing a portion of the oxide to enter the tube; repeating the operation until the tube is nearly full: when the mouth is no longer too hot it should be closed with a dry cork, and allowed to cool. Meantime the interior of the combustion tube is to be dried completely by heating each portion of it in succession, beginning at the open end, whilst drawing air through it by means of a narrower tube passed down just beyond the heated part. When every part has thus been dried, the combustion tube is to be corked and allowed to cool.

Five or six grains, or about 0·3 grm., of the substance are usually enough for analysis. The watch glasses containing the substance should be carefully weighed, and after the requisite quantity has been taken out and mixed with the cupric oxide in the manner described below, the glasses must be closed with the clip and again weighed. Great care should be taken in charging the combustion tube. Cupric oxide to the depth of about an inch (2·5 centimetres) is first poured into it; after which a small quantity of the oxide is to be put into a hemispherical glass dish resting on a sheet of glazed paper, then the substance to be analysed, then more oxide. This dish must be thoroughly cleaned and rinsed out with a little of the oxide previously to being used, and the interior of it should on no account be touched with the fingers, as the finer portions of the cupric oxide would be sure to adhere in those places. The mixture must be made quickly and carefully by means of a thin flexible steel spatula, as much oxide being employed as will be sufficient to fill a little more than half the combustion tube. The dish is now to be taken in the palm of the left hand, and the mixture introduced by scooping it up into the tube with a peculiar turn of the wrist, which can easily be acquired after a little practice. The last portions of the mixture are most easily introduced by transferring them to a highly glazed card, and pouring them from it directly into the combustion tube. The dish is then washed out two or three times successively with small quantities of the oxide in order to remove the last traces of the mixture, the washings being introduced into the tube in the manner just described: the combustion tube is finally to be filled up with pure cupric oxide to within two inches (5 centimetres) of the extremity. Instead of a glass dish and steel spatula, an ordinary porcelain pestle and mortar may be used, but it is not so convenient: sometimes also when many tubes have to be filled, and it is desired to save time, the mixture, washings, &c., may be poured into the combustion tube through a clean bright copper funnel.

The proportions of the mixture are represented at 1, fig. 385, in which the portion from the tail of the tube to the letter *a* consists of pure cupric oxide; that from *a* to *b* of the mixture; that from *b* to *c* of the rinsings of the mortar, and the pure oxide. The tube having been closed by a cork is to be tapped gently on the table, so as to clear the tail-like prolongation, and make an airway above the oxide from end to end.

Bunsen has introduced some slight modifications of Liebig's method which are very convenient, especially for hygroscopic substances. The substance to be burnt is weighed in a long narrow tube, which can be closed by a cork or ground stopper, and from which it is transferred directly to the combustion tube. About 4 inches (10 centimetres) of oxide are introduced into the latter, the compound to be burnt is then poured in from the weighing tube, then 4 inches more of cupric oxide. In order thoroughly to mix the substance with the oxide, the two are stirred up together in the combustion tube by means of a long bright iron wire, having one end pointed and twisted like a corkscrew, and the other bent into a ring to serve as a handle. Finally the tube is filled up with pure oxide as usual.

The drying tube *e*, fig. 386, having been accurately weighed, is next to be fitted to the caoutchouc plug or dried perforated cork, and connected by it air-tight to the tube *a b c*. The combustion tube is now placed in the furnace, and the potash apparatus *f*, also previously weighed, is attached to the drying tube by means of a connecting piece of caoutchouc, care being taken that the largest bulb is on the arm connected with the drying tube. If Liebig's potash bulbs be used they should be slightly inclined by placing a cork under the end of the horizontal portion nearest the open extremity. Matters being thus arranged, the next thing is to ascertain if the whole apparatus be tight, and for this purpose the air in the large bulb is to be gently heated so as to expel a few bubbles; if, on cooling, the liquid rises in the limb and maintains its elevation steadily for a few minutes, the combustion may safely be begun. A screen of iron plate is hung over the end of the furnace nearest the absorption apparatus to protect the cork, care being taken that the heat never rises so high as to scorch it, or falls so low as to allow of the condensation of moisture in that part of the tube which projects from the furnace.

The portion of the tube nearest the cork, where the pure cupric oxide lies, is first heated; as soon as it is red hot and the escape of air due to expansion has ceased, about an inch more of the tube may be heated; when this has become red hot, heat is applied to a fresh portion, proceeding gradually and slowly in this manner to heat the whole length of the tube. When the heat reaches the rinsings of the dish, a little carbonic anhydride and aqueous vapour are evolved, but as soon as the mixture of the substance with the cupric oxide begins to decompose the gas comes off much more rapidly, and the heating should be so regulated that not more than one or two bubbles pass into the potash apparatus in a second. At first only a small portion of the escaping gas is absorbed, but when the substance is fairly undergoing decomposition, and the atmospheric air in the apparatus has been expelled, the gas is almost entirely taken up by the potassic hydrate solution. Even after the whole tube is ignited, the heat must be continued until gas ceases to be disengaged. The liquid will then gradually recede into the large bulb; as soon as this is observed, the gas should be turned off, or the charcoal removed from the tail of the tube, and when the solution of potassic hydrate has risen sufficiently to fill half the large bulb, the tip of the tail must be nipped off: gentle suction is now to be effected by means of the aspirator or the mouth adapted to the free extremity of the potash apparatus by a tube of vulcanized caoutchouc, and air drawn through the combustion tube in order to displace the carbonic anhydride and aqueous vapour which the apparatus contains.

If the combustion tube is not of very hard glass, and it be allowed to become very hot, the pressure of the gas may sometimes be sufficient to distend the tube, and even to blow a hole in the side. This necessarily renders the experiment valueless, and in order to avoid such a mishap it is advisable to render the pressure in the interior of the combustion tube the same as that of the atmosphere, or even to produce a partial vacuum. This is easily effected by means of an aspirator, a simple form of which is represented in fig. 385; *l* is a tubulated bottle filled with water, and connected with the absorption apparatus, *h k*, by means of a caoutchouc tube; from the tubulure a flexible tube passes into the beaker *o*, placed in the bottom of a funnel, *n*, supported on the ring of a tripod stand, by which it can be raised or lowered. The tube *m* serves as an indicator of the amount of exhaust produced by the aspirator, which is the difference between the level of the water in *l* and that in *o*, or, what is the same thing, the difference between the surface of the water in the bottle *l* and that in the tube *m*. This column should be somewhat greater than that which the gas has to overcome in passing through the liquid in the potash bulbs.

Dumas prefers to connect the extremity of the combustion tube with a drying tube, and this again with a receiver containing oxygen, which gas is carefully driven over the contents of the tube in the manner shown in a former volume, fig. 306, Part II, p. 123. This renders the operation somewhat more complicated, but it is more exact, especially for compounds where the proportion of carbon is great. The tube for supplying oxygen is easily adjusted to the combustion tube by drawing out the tail horizontally instead of obliquely, and fitting it on by a caoutchouc connector, care being taken to screen the junction from the influence of heat. Instead of merely completing the operation by passing oxygen through the tube in the manner described, it is very convenient when many combustions have to be made to burn the substance in a platinum boat, in a current of oxygen, as shown in fig. 385. For this purpose the combustion tube is open at both ends, one end being connected with the usual absorption apparatus, *h k*, the other with a drying apparatus, consisting of a series of tubes, *b*, containing soda lime or potassic hydrate, and the bulb *c*, containing sulphuric acid, through which a current of air or oxygen can be transmitted at pleasure from the gasholder *a*. About two-thirds of the length of the combustion tube nearest the absorption apparatus is filled with granular cupric oxide, which is kept in its place by a plug of asbestos. The substance to be burnt is contained in a platinum boat, which is pushed into the tube close to the asbestos plug. As soon as the fore part of the tube is heated to redness, and the heat is approaching that part where the platinum boat is placed, a gentle current of oxygen is passed, and the substance cautiously burnt. When this is completed the oxygen is turned off, and a slow current of atmospheric air passed until the apparatus is cool. With this method the same tube will answer for several combustions.

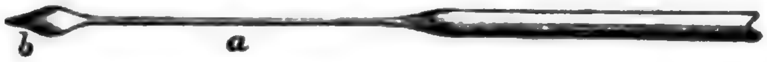
The absorption apparatus is now disconnected, and allowed to cool. In about an hour the drying tube *e* may be weighed; one-ninth of the gain which it has experienced indicates the quantity of hydrogen contained in the compound analysed; the potash apparatus *f*, is also to be weighed, and three-elevenths of what it has gained shows the quantity of carbon. The deficiency is reckoned as oxygen.

The cupric oxide, after having been used several times, requires to be re-oxidized by moistening it with nitric acid, and igniting it as before described.

In cases where chlorine, bromine, iodine, or sulphur is present in the compound to be analysed, *plumbic chromate*, $PbCrO_4$, may be advantageously substituted for the cupric oxide, as chloride, bromide, and iodide of copper are somewhat volatile, and would be carried by the current of gas into the drying tube, whilst with cupric oxide the sulphur present would pass over as sulphurous anhydride into the potash bulbs. The chromate is also useful with substances difficult of combustion, since by a bright red heat alone it gives off a portion of its oxygen; moreover, it has the advantage of being less hygroscopic than cupric oxide. It is easily prepared by precipitating potassic chromate or dichromate with a solution of plumbic acetate, and should be well washed and heated to incipient fusion before being used for analysis. It is then reduced to fine powder, and employed in the same way as cupric oxide, but it is not necessary to have the combustion tube so long, and the *anterior* portion of the tube should never be heated higher than a dull red, so as to avoid fusing the chromate there. It is frequently advantageous to mix the substance, especially if very difficult to burn, with plumbic chromate and a small quantity of potassic dichromate, $K_2Cr_2O_7$, which fuses readily and ensures its complete combustion, the rest of the tube being filled with plumbic chromate. The potassic dichromate employed for this purpose should always be carefully recrystallized to make certain that no organic matter is present.

(1035) *Analysis of a Liquid not containing Nitrogen.*—If the liquid be *volatile*, a piece of tube rather less than a quarter of an inch or 6 millim. in diameter is to be heated in the blowpipe flame, and drawn out into a capillary portion, *a*, fig. 387, about four inches (10 centimetres) long: about a quarter of an inch below this the tube is to be sealed, and the little piece of tube, *b*, thus left connected with the capillary part, heated and blown into a small bulb about as big as a pea; this is to be cut off, leaving a capillary neck of about two inches (5 centimetres) long. Having made a sufficient number of these small bulbs, two of them, which it has been ascertained will freely enter the combustion-tube, are to be accurately weighed; a little of the liquid to be analysed is to be put into a small tube, and the capillary neck of the bulbs inverted into the liquid. The bulbs are then to be warmed by the flame of a spirit-lamp, so as to expand and drive out a portion of the air; on cooling, the liquid will enter the bulbs, which should be about three-fourths filled. The necks are now to be sealed by the blowpipe flame, and the bulbs again weighed; the increase of weight gives the quantity of the liquid which is to be analysed. The cupric oxide having been heated and allowed to cool with the usual precautions, about an inch and a half (36 millimetres) of the combustion tube is to be filled with pure oxide; next a scratch is to be made with a file or knife across the capillary neck of one of the bulbs, and the bulb having been placed in the tube, the neck is to be broken by pressure against the glass, and the broken portion of the neck to be dropped in with the bulb; dried cupric oxide is then to be poured in to the depth of two inches more; the second bulb is to be introduced in the same manner as the first, and the tube is to be filled up with oxide; after which it is to be corked and struck smartly upon its side on the table, to secure free air-way. The absorption apparatus is now attached and the combustion tube adjusted in the furnace, and the first half of the tube gradually heated; when this is red-hot, the liquid must be volatilized by cautiously heating the part of the tube where the nearest bulb lies, taking especial care not to raise the temperature too rapidly: when by degrees all the liquid in the first bulb has been expelled, the other is to be proceeded with in like manner; the whole length of the tube is finally heated, and the gases are driven out of the apparatus by means of a current of oxygen in the manner already described.

FIG. 387.



This precaution is necessary with substances which contain a relatively large proportion of carbon, as they would otherwise escape complete combustion. Instead of employing oxygen gas, some finely pulverized, carefully dried potassic chlorate may be mixed with about four times its weight of cupric oxide, and about an inch of the combustion tube near *a* (fig. 386) may be filled with it; the tail-like prolongation may in this case be dispensed with. At the close of the operation, instead of sucking air through the apparatus, heat is to be very cautiously applied to the chlorate; the oxygen that is evolved burns the last traces of carbon and displaces the gas and aqueous vapour contained in the tubes. The heat must not be too suddenly applied, for if it be, a portion of the chlorate is apt to be carried forward mechanically, a circumstance which constitutes the chief objection to its use.

If the liquid be *not volatile* it may be weighed in a small tube the weight of which, when empty, is known, and after the tube with its contents has been introduced into the combustion tube, the liquid is to be distributed over the sides of this tube; or it may be weighed in bulbs like volatile liquids, and these after their introduction into the combustion tube, are crushed by dropping on them a short pointed piece of glass rod about an inch long, subsequently filling in the cupric oxide in the usual manner.

(1036) *Analysis of a Body containing Nitrogen.*—The presence of nitrogen in an organic compound may generally be ascertained by mixing a small quantity of it with some solid potassic hydrate, and heating it in a test tube: if nitrogen be present, vapours of ammonia will be evolved. The nitrogen in certain organic substances, however, cannot be readily detected in this manner: for instance, in cyanogen compounds, nitro-substitution compounds, and such bodies as indigo and the alkaloids which yield volatile organic bases by the action of an alkali. The best method in these cases is to heat some of the compound under examination with metallic sodium. A violent action usually takes place, accompanied by deposition of carbon, whilst the nitrogen and a portion of the carbon combines with the sodium, forming sodic cyanide. On dissolving the product in water, filtering, and adding a few drops of a mixed solution of ferric and ferrous sulphates, potassic ferrocyanide is formed. The addition of an excess of hydrochloric acid dissolves the precipitated oxide of iron, which now forms Prussian blue with the ferrocyanide. The presence of very small quantities of nitrogen can be ascertained by these means.

When nitrogen is present, two separate analyses are required: the first, to determine the proportion of carbon and hydrogen; and the second, to ascertain the amount of nitrogen. In making a determination of the carbon and hydrogen in bodies containing nitrogen by burning them with cupric oxide, a variable proportion of the lower oxides of nitrogen is formed, which being absorbed by the calcic chloride, or by the potassic hydrate, would render the analysis incorrect. A slight variation in the method employed becomes necessary in order to prevent this. The combustion tube must be longer than when there is no nitrogen present, and should be charged as usual to within 6 inches (15 centimetres) of the opening, finally introducing about 4 inches (10 centimetres) of copper turnings, or a roll of fine copper wire gauze of the same length. The copper, just before being used, should be heated to redness in the air, and then reduced in a current of hydrogen. The apparatus having been arranged as before directed, the copper turnings are to be brought to a full red-heat, and the analysis cautiously conducted in the ordinary manner. As the oxides of nitrogen pass slowly over the ignited copper they are decomposed, the oxygen combining with the copper, whilst the nitrogen escapes. The amount of carbon and hydrogen is determined exactly as in the method previously described.

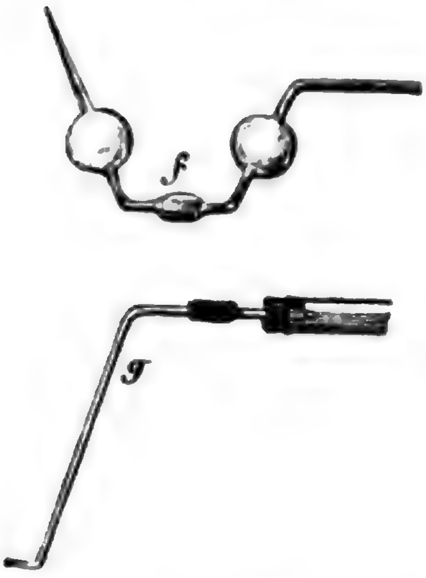
(1037) *Method of Varrentrapp and Will.*—A very accurate method for ascertaining the proportion of nitrogen is that devised by Varrentrapp and Will; the fundamental fact upon which it is based being the observation of Gay-Lussac that most azotized matters, when heated with a large excess of potassic or sodic hydrate, give off the whole of the nitrogen in the form of ammonia. In order to render this method available for the purposes of analysis, the subjoined precautions are requisite

A mixture of two parts of quicklime and one of sodic hydrate is prepared by slaking well-burned lime with the necessary quantity of a solution of sodic hydrate, and evaporating the whole to dryness; the mass is then ignited, pulverized as quickly as possible, and transferred to well-closed bottles, in order to exclude carbonic acid and moisture. A mixture of equal parts of sodic carbonate and of slaked lime answers even better, and is much less troublesome to prepare than the above; sodic carbonate for this purpose being easily obtained by heating the commercial "bicarbonate" until it ceases to give off aqueous vapours (S. W. Johnson, *Ann. Chem. Pharm.* clxix. 69).

When an analysis has to be made, the substance under examination is intimately mixed in a glass dish or warm mortar with a portion of this alkalized lime, or *soda-lime* as it is generally termed, in a manner similar to that already described for the determination of the carbon and hydrogen in a compound. In this case, however, it is not necessary to be so careful in avoiding the absorption of moisture during the operation of filling the tube.

The mixture having been introduced into the combustion tube, a plug of asbestos which has been recently ignited is inserted in order to prevent any of the mixture being carried forward mechanically into the apparatus through which the gases are made to pass. On heating the combustion tube in the ordinary way, and with the usual precautions, the substance is decomposed, and the whole of the nitrogen escapes as ammonia. The drying-tube and the potash apparatus are not used, but the ammonia is collected in a bulb-tube of the form represented at *f*, fig. 388, which is connected air-tight with the combustion tube by means of a good cork. The bulbs *f* are charged with hydrochloric acid of sp. gr. 1·1 which has been previously tested and found to be *free from ammonia.*

FIG. 388.



When the operation is complete, absorption will take place, and the liquid will rise in the bulb nearest the fire; at this moment the tail of the combustion tube should be nipped off, and air carefully drawn through the apparatus in the usual way. When the combustion is completed, the contents of the bulb-tube are to be emptied into an evaporating dish, and the bulbs washed out several times with water; solution of platinic chloride is then added in excess, and the whole evaporated to dryness on a water-bath. The residue when dry is digested with a mixture of two parts of alcohol, sp. gr. 0·833, and one of ether, which dissolves the excess of platinic chloride, and leaves the double chloride of platinum and ammonium in a crystalline form: this is now collected on a weighed filter, and thoroughly washed with the mixture of alcohol and ether. The precipitate and filter may be dried at 100° (212° F.), and the amount of nitrogen calculated from the observed weight of the ammonic platinic chloride, 446·1 parts of which correspond to 28 of nitrogen, or 100 parts to 6·277 of nitrogen. As, however, in some instances, volatile bases other than ammonia are produced during the combustion of nitrogenous organic compounds, and these also form double salts with platinic chloride and hydrochloric acid, a source of error would be introduced if the amount of nitrogen were calculated from the weight of the dry double salt. It is therefore always advisable to ignite this, and calculate the nitrogen from the weight of the residual metallic platinum, 197·1 of which correspond to 28 of nitrogen, or 100 to 14·206 of nitrogen. Instead of collecting the ammonia in hydrochloric acid, it may be condensed in a known volume of standard sulphuric acid, or solution of oxalic acid. About 150 grains, or 10 c.c. of an acid of which 100 parts will neutralize 1·7 parts by weight of ammonia, will answer the purpose. The acid liquor is then to be washed out of the bulbs *f*, diluted, and carefully neutralized by means of a corresponding standard solution of sodic hydrate. By this means the amount of acid which has been neutralized by the ammonia is ascertained, and the nitrogen present in the substance burnt can easily be calculated from it.

(1038) *Method of Dumas.*—The foregoing method of determining nitrogen answers for nearly all cases excepting those in which the element occurs in a cyanide or a nitro-substitution compound, when it must be determined by volume, and its weight thence deduced. For this purpose the process of Dumas is the most trustworthy:—A combustion tube of about 30 inches (75 centimetres) long is employed, not drawn out into a tail, but sealed with a rounded extremity; about 6 inches (15 centimetres) of the tube are filled with dry hydric sodic carbonate, $NaHCO_3$, then an inch or two of pure cupric oxide; after this the mixture of the substance with cupric oxide is added, and covered as usual with a layer of pure oxide, finally, the last 3 or 4 inches of the tube are filled with clean copper, as already directed, with a view of decomposing any oxides of nitrogen which might be formed. Instead of hydric sodic carbonate, a mixture of equal molecular weights of dried sodic carbonate and potassic dichromate may be employed, which has the advantage of giving off carbonic anhydride free from aqueous vapour when heated. It is, however, unnecessary to be particular in excluding moisture whilst filling the tube.

After gently tapping the tube so as to make an air-way over the cupric oxide, it is connected with a bent delivery tube *g*, fig. 388, and placed in the combustion furnace, the end of the delivery tube dipping into a small mercurial trough. About 2 inches (5 centimetres) of the closed end of the tube are now heated, when a portion of the carbonate is decomposed, and the evolved carbonic anhydride gradually expels the air from the tube. In a short time it will be found that the gas escaping from the delivery tube is completely absorbed when passed up into a solution of potassic hydrate contained in an inverted test tube, and consists, therefore, of pure carbonic anhydride. A graduated cylinder filled one-third with a concentrated solution of potassic hydrate and two-thirds with mercury is now inverted over the delivery tube, and the combustion proceeded with in the usual way, commencing at the copper turnings.

When the part of the combustion tube containing the matter for analysis is red-hot throughout its entire extent, heat is gradually applied to the carbonate still remaining undecomposed, and the last portions of gas furnished by the combustion are driven into the receiver by the carbonic anhydride which is disengaged.

The products of the combustion are water, carbonic anhydride, and nitrogen; the two former are retained by the solution of potassic hydrate, and the nitrogen remains in the graduated cylinder in the gaseous state. The tube is now transferred to a deep vessel of water, allowing the mercury to fall out and become replaced by the water. It is then adjusted so that the level of the liquid inside and outside the tube are the same, and after allowing it to stand for an hour or two, in order that the whole apparatus may be of the same temperature as the atmosphere, the height of the barometer and thermometer must be carefully noticed, and since the gas will be saturated with moisture, its volume must be corrected for temperature, pressure, and aqueous vapour. As a litre of dry nitrogen at 0° C. and 760 mm. barometric pressure weighs 1·25616 grm., or 100 cubic inches of nitrogen at 60° F. and under a pressure of 30 inches of mercury weigh 30·137 grains, it is easy to calculate the weight of the known volume of nitrogen, and consequently the proportion of that element present in the compound analysed.

(1039) *Method of Relative Volumes.*—When the quantity of nitrogen present is not less than one-fourth of the weight of the carbon contained in the compound, its proportion may be determined by conducting the combustion just as if we were going to ascertain the proportion of carbon and hydrogen; but, instead of condensing the carbonic anhydride and weighing it, the evolved gases are collected over mercury. A bent gas-delivering tube, *g*, fig. 388, is used instead of the usual apparatus for the absorption of water and carbonic anhydride. In this case, as soon as the fore part of the tube containing the metallic copper and pure oxide is red hot, the combustion of the substance should be commenced at the closed extremity of the tube, so as to expel the atmospheric air by means of a portion of gas generated from the substance. The remainder is collected in successive portions in several graduated tubes, and by agitating the gas in each of these with a solution of potash, the proportion of nitrogen to the carbon can be at once determined, since equal volumes of carbonic anhydride and nitrogen represent equal atomic proportions of carbon and nitrogen. It is not necessary in this case to weigh accurately the quantity of material employed.

Experience has shown that in the preceding processes for organic analysis, the quantity of hydrogen deduced from the results is always slightly in excess, usually from 0·1 to 0·2 parts in 100; whilst unless oxygen or plumbic chromate be employed, the carbon is sometimes deficient to the same extent. A deficiency of carbon also occurs if the ash contains carbonates of the metals of the alkalies or of the earths.

(1040) *Determination of Sulphur, Phosphorus, and Arsenicum.*—One of the methods employed for ascertaining the amount of sulphur in an organic compound, consists in mixing 1 part of the substance for analysis with 10 parts of nitre, 2 of dried sodic carbonate, and 30 of pure sodic or potassic chloride, and heating the mass to redness in a tube of hard glass. The sulphur is thus converted into sulphate. The object of adding the sodic chloride is simply to moderate the violence of the deflagration. The residue is dissolved in water slightly acidified with hydrochloric acid, and the sulphuric acid is then determined in the usual way by precipitation with baric chloride. If phosphorus or arsenicum be present, it will remain in the acid liquor in the form of phosphoric or arsenic acid. Its amount may be determined by adding sulphuric acid in order to throw down the excess of barium salt; then filtering, supersaturating with ammonia, and adding an ammoniacal solution of magnesic sulphate: the phosphoric or arsenic acid is precipitated as ammonic magnesic phosphate or arseniate, and can be collected in the usual manner. The sulphur in organic compounds may also be determined by burning them in a combustion tube with a mixture of mercuric oxide and pure sodium carbonate in a manner similar to that employed for the estimation of nitrogen by Varrentrapp and Will's method. A little pure oxide of mercury is introduced into the closed end of the tube, which is heated at the completion of the operation so as to pass a current of oxygen through the tube to insure the complete oxidation of the sulphur to sulphate. The contents of the tube, when cold are dissolved in water and the amount of sulphuric acid produced estimated in the usual way.

Another method, and one less liable to error, consists in sealing up the substance in a tube with strong nitric acid of sp. gr. 1·52 and heating it from four to twenty-four hours at 150° to 200° (302° to 392° F.); the amount of sulphate can then be determined in the usual way, and the phosphate or arseniate after neutralization with ammonia.

When sulphur is present, certain precautions are necessary to prevent error in the estimation of the amount of carbon, since a portion of the sulphur becomes converted during the process of combustion with cupric oxide into sulphurous anhydride, and this would be condensed by the potassic hydrate along with the carbonic anhydride, which would then be estimated in excess. This may be avoided by interposing a short tube filled with plumbic peroxide between the tube of calcic chloride and the potash bulbs; the sulphurous anhydride is by this means absorbed, uniting with the plumbic peroxide and forming plumbic sulphate, $PbO_2 + SO_2$ becoming $PbSO_4$: it is far better, however, to employ plumbic chromate instead of cupric oxide, when the sulphur is retained as plumbic sulphate.

(1041) *Determination of Chlorine, Bromine, and Iodine.*—When a substance containing chlorine is burnt with cupric oxide, cuprous chloride is formed and would be carried forward into the chloride of calcium tube and condensed there; moreover, if a current of oxygen is used, free chlorine is obtained which, passing into the potash apparatus, would be absorbed there and render the analysis valueless. These sources of error, however, may be entirely avoided by introducing a coil of silver foil 2 or 3 inches long (5 to 8 centimetres) into the anterior portion of the tube, which retains the chlorine as argentic chloride. Even when plumbic chromate is used, it is always advisable to employ the silver foil, especially with substances containing a large percentage of chlorine. These remarks apply equally to organic compounds containing bromine or iodine. If the quantity of chlorine, or of any other halogen, is to be estimated, the substance for analysis is mixed with about 10 times its weight of pure lime, and introduced into a narrow tube of Bohemian glass 10 or 12 inches (25 or 30 centim.) long, and sealed at one end. The tube is filled up with fragments of pure lime, and gradually brought to a red heat, commencing at the open extremity. When the combustion is complete, and the tube cold, its contents are transferred to a beaker containing distilled water, afterwards carefully washing out the tube, first with water and then with dilute nitric acid. Nitric acid is now cautiously added to the mixture until the lime is dissolved, taking care only to employ a slight excess of nitric acid, after which the liquid is filtered, and the chlorine, iodine, or bromine precipitated by means of argentic nitrate.

The determination of these elements may also be very readily made by the method proposed by Carius (*Deut. Chem. Ges. Ber.*, III. 697) of heating the compound with nitric acid and silver nitrate in a sealed tube, to a high temperature, in a manner similar to that already described for the estimation of sulphur. The substance to be analysed is enclosed in a weighed glass bulb, which is broken after it is sealed up along with the nitric acid. The argentic chloride produced is collected and weighed along with the broken bulb, the weight of the latter being subtracted afterwards As however the glass of which the bulbs are made may be partially dissolved by the nitric acid, which would tend to diminish the apparent amount of the halogen, it is better, in order to avoid this source of error, to place the substance in a short piece of glass tube sealed at one end and closed by a ground stopper, instead of enclosing it in a glass bulb. After the operation is over, it is easy to separate the argentic compound from the tube and stopper. The results obtained with iodine compounds are generally too low, in some instances as much as 1 per cent. According to Linnemann, this is probably due to the solubility of argentic iodide in an acid solution of argentic nitrate.

(1042) *Determination of other Elements.*—The other elements occasionally met with in organic substances are determined by the ordinary methods, but it is generally necessary to oxidize or incinerate the substance in the first place. This operation should always be performed at a low temperature, which need not exceed a barely visible red, as otherwise, if alkaline chlorides be present they would be partially volatilized.

General Remarks on the Discrimination of the Gases.

(1043) The principal bodies which are gaseous at the mean temperature of the atmosphere are about 35 in number. Several of these compounds are met with in the uncombined form in the atmosphere, either uniformly, or under particular circumstances not of unfrequent occurrence; these gases are oxygen, nitrogen, carbonic and sulphurous anhydrides, hydrosulphuric acid, ammonia, and occasionally carbonic oxide and methane or methylic hydride. Generally speaking, the different gases, when pure, are readily distinguished from each other by some well-marked physical or chemical property. The few gases which are coloured are at once indicated by the peculiarity of their tint, conjoined with their characteristic odour: in this manner peroxide of nitrogen, chlorine, hypochlorous and chlorous anhydride, chloric peroxide, and vapour of bromine are at once recognised.

Many gases have a peculiar and characteristic odour. Some of the most important, however, including oxygen, nitrogen, hydrogen, carbonic anhydride, carbonic oxide, methane or light carburetted hydrogen, ethylene or olefiant gas, and nitrous oxide possess little or no odour, and require other means for discriminating them from each other.

(1044) In order to aid the operator in distinguishing the different gases from each other, Thénard divided them into four groups, the arrangement being dependent upon the action of a solution of potassic hydrate upon them, conjoined with the occurrence or the absence of combustion on the application of a lighted match to the gas. The experiment is made by admitting a few drops of a solution of potassic hydrate into a test-tube filled with the gas, and standing over mercury: on agitating the contents of the tube, it is immediately obvious whether any absorption occurs. The application of a lighted match to another small tube filled with the gas shows whether it be inflammable, or whether it extinguishes or supports combustion.

The four groups of gases which are distinguished by the application of these tests are the following:—

1. Gases which are absorbable by potassic hydrate, but which are not inflammable.
2. Gases absorbable by potassic hydrate, but which are inflammable.
3. Gases not absorbable by potassic hydrate, and not inflammable.
4. Gases not absorbable by potassic hydrate, which are inflammable.

We proceed to point out briefly the characters of the members of each group.

(1045) 1.—*Gases which are absorbable by Potassic hydrate, but are not inflammable*; these are 15 in number :—viz.,

1. Hydrochloric acid
2. Hydrobromic acid
3. Hydriodic acid
4. Silicic fluoride
5. Boric fluoride
6. Boric chloride
7. Carbonic oxydichloride
8. Sulphurous anhydride
9. Nitrous anhydride
10. Chloric peroxide
11. Chlorous anhydride
12. Hypochlorous anhydride
13. Chlorine
14. Carbonic anhydride
15. Cyanic chloride.

Of these gases each of the first eleven reddens litmus-paper, when moistened and plunged into it. Hypochlorous anhydride and chlorine destroy its colour, and bleach it entirely. Carbonic anhydride is nearly without action, and cyanic chloride produces no effect upon its colour. The first six gases fume strongly when mixed with the air, owing to their action on the moisture which it contains: the solutions in water of hydrochloric, hydrobromic, and hydriodic acids are immediately distinguished by the usual tests for them. Each gas also presents certain peculiarities—viz, 1.—A small quantity of chlorine produces no change in the hydrochloric acid; 2.—In hydrobromic acid it occasions the separation of red fumes of bromine; and 3.—In hydriodic acid violet fumes of iodine appear. 4.—Silicic fluoride is recognised by the gelatinous deposit of silica which water produces when the gas is brought in contact with this liquid. 5.—Boric fluoride produces a gelatinous precipitate in a solution of potassic hydrate, but not in pure water. 6.—Boric chloride is decomposed by water into hydrochloric and boracic acids, which may be recognised in the solution by the appropriate tests. 7.—Carbonic oxydichloride has a peculiar, pungent odour, and is decomposed by water into hydrochloric acid and carbonic anhydride. 8.—Sulphurous anhydride is immediately recognised by the suffocating odour of burning sulphur: it is absorbed by plumbic peroxide, and a white plumbic sulphate is formed. 9.—Nitrous anhydride is sufficiently characterized by its colour and peculiar odour; and 10.—The same may be remarked of chloric peroxide. 11.—Chlorous anhydride has a greener tinge than the chloric peroxide, and it yields a bright yellow solution when dissolved in water. 12.—Hypochlorous anhydride has the odour of the bleaching compounds of chlorine with the alkalies and earths, and it rapidly destroys vegetable colours: these three oxides of chlorine detonate by the application of a temperature below that of boiling water. 13.—Chlorine is distinguished by its greenish yellow colour and remarkable odour, by its bleaching action on vegetable colours, and by its sparing solubility in water, which only takes up about twice its bulk of the gas. 14.—Carbonic anhydride extinguishes flame, renders lime-water turbid, and is soluble in about its own bulk of water. 15.—Cyanic chloride is recognised by its pungent odour, and its peculiarly irritating effect on the eyes.

(1046) 2.—*Gases absorbable by Potassic hydrate and inflammable*; these are only 4 in number:—viz.,

1. Sulphuretted hydrogen
2. Seleniuretted hydrogen
3. Telluretted hydrogen
4. Cyanogen.

These gases are recognised with great facility. 1.—Sulphuretted hydrogen has a peculiar odour of putrid eggs; it burns with a blue flame, often attended with a deposit of sulphur; it blackens paper soaked in a solution of plumbic acetate, and is decomposed by moist chlorine, with separation of sulphur; water dissolves about twice its bulk of the gas. 2.—Seleniuretted hydrogen has an odour analogous to that of the preceding gas; its aqueous solution gradually deposits selenium in the form of a red amorphous precipitate; it precipitates salts of zinc of a flesh-red colour. 3.—Telluretted hydrogen is also decomposed by chlorine, tellurium being set free, and subsiding as a brown powder. 4.—Cyanogen burns with a rose-edged purple flame; it has a penetrating characteristic odour. If mixed with an equal volume of oxygen, and a red-hot platinum wire be suspended in the mixture, red nitrous fumes are produced by the oxidation of the nitrogen contained in the gas.

(1047) 3.—*Gases not absorbable by Potassic hydrate and not inflammable;* of these also there are four—viz.,

1. Oxygen
2. Nitrous oxide
3. Nitrogen
4. Nitric oxide.

1.—Oxygen is at once distinguished from all other gases by its property of kindling a glowing match, by its power of producing red fumes when mixed with nitric oxide, and by its insolubility in water when agitated with it. It is absorbed by moistened phosphorus, by a solution of cuprous oxide in ammonia, rendering the colourless solution deep blue, and by a solution of pyrogallic acid in potassic hydrate, the mixture becoming of an intense bistre colour. Solutions of the sulphides of the alkali-metals also absorb oxygen rapidly. 2. Nitrous oxide, although it rekindles a glowing match, is dissolved when agitated with water. 3.—Nitrogen extinguishes the flame of burning bodies; it is insoluble in water, and does not render lime-water turbid. 4.—Nitric oxide is instantly recognised by the red fumes which it occasions when mixed with air or free oxygen; it is immediately absorbed by a solution of ferrous sulphate, giving the liquid a deep brown colour when oxygen is present.

(1048) 4.—*Gases not absorbable by Potassic hydrate, which are inflammable:—*

1. Hydrogen
2. Methane, or methylic hydride, and its homologues, ethane, propane, and butane or tetrane
3. Olefiant gas, or ethylene, and its homologues, propylene and butylene
4. Acetylene and allylene
5. Phosphuretted hydrogen
6. Arseniuretted hydrogen
7. Carbonic oxide.

1.—Hydrogen is inodorous, if pure; it burns with a feebly luminous flame, and if mixed with half its volume of oxygen, produces water either by the transmission of an electric spark, or by the action of a ball of spongy platinum. 2.—Methane burns with a yellowish flame; it is not acted upon if mixed with chlorine over water and screened from light, and is not dissolved by fuming sulphuric acid. 3.—Ethylene, or its homologues, when mixed with an equal volume of chlorine, even in the dark becomes condensed to an oily liquid which is insoluble in water; it is also absorbed by antimonic pentachloride, and by Nordhausen sulphuric acid: it burns with a brilliant smoky flame. 4. Acetylene may be separated by taking advantage of the property it possesses of being absorbed by an ammoniacal solution of cuprous chloride. The red precipitate thus obtained, is decomposed by hydrochloric acid, yielding the hydrocarbon in the free state. 5.—Phosphuretted hydrogen is distinguished by its peculiar alliaceous odour: it burns with a luminous flame, producing white fumes of phosphoric anhydride; solutions of the salts of copper, silver, and mercury dissolve it and form brown precipitates. 6.—Arseniuretted hydrogen is decomposed if passed through glass tubes heated nearly to redness, a ring of arsenicum being deposited: it burns with a peculiar white flame, and deposits a brown stain of arsenicum on cold bodies introduced into the burning jet. It is extremely poisonous, and has a peculiar odour of garlic. It may be distinguished from antimoniuretted hydrogen by methods previously described (841). 7.—Carbonic oxide burns with a pale blue flame, producing carbonic anhydride; it is insoluble in water, and is dissolved by a solution of cuprous chloride in hydrochloric acid.

(1049) *General Principles of the Analysis of a Mixture of Gases.*—In a mixture of gases a qualitative examination must be made as a preliminary step, in order to ascertain what gases are present. It is of course needless to search for those which condense or decompose each other. Ammonia, for example, would not be found in a mixture which contained hydrochloric, hydriodic, or hydrobromic acid gases, nor in the presence of sulphurous or nitrous anhydrides. Oxygen would not occur in a mixture in which nitric oxide was present. Neither could free chlorine or its oxides co-exist with hydriodic or hydrobromic acid, nor with ethylene, nor with the compounds of hydrogen with sulphur, selenium, tellurium, phosphorus, or arsenic: chlorine and its oxides are equally incompatible with ammonia.

The complete analysis of a mixture of different gases is one of the most delicate and difficult branches of chemical analysis, and it is not intended to attempt to give more than an idea of the principles on which such an operation is conducted, and the manner in which it is effected.

As an illustration of the method of proceeding we may take a case of frequent occurrence: viz., the determination of the composition of a sample of coal-gas. In this case, the ingredients which may be present are numerous. These are—1, hydrogen; 2, ethylene or olefiant gas and other unsaturated hydrocarbons; 3, methane or light carburetted hydrogen; 4, carbonic oxide; 5, carbonic anhydride; 6, sulphuretted hydrogen; 7, ammonia; 8, oxygen; and 9, nitrogen, the last two derived from the atmosphere.

A qualitative examination is made thus:—the proportion of ammonia and of sulphuretted hydrogen is usually very minute, and in most cases these gases must be sought for by placing the tests for their presence for some time in a current of the coal-gas. In searching for ammonia, a piece of moistened litmus-paper, feebly reddened, is placed for a minute in a jet of the issuing gas: if the blue colour be restored, ammonia is present. Paper soaked in a solution of plumbic acetate may be subjected to a similar trial: if it turn brown, sulphuretted hydrogen is present. The presence of oxygen is detected by admitting a bubble of nitric oxide into a tube filled with the gas under trial, and looking through the tube obliquely upon a sheet of white paper; very small traces of oxygen may thus be detected by the red tinge produced, owing to the formation of peroxide of nitrogen. Carbonic anhydride may be detected by the turbidity which it produces in lime-water or in a solution of basic plumbic acetate, if thrown up into the gas whilst standing in a tube over mercury. The other gases are certain to be present, in greater or less quantity. The sulphuretted hydrogen and ammonia are too small in amount to be quantitatively determined; but supposing that oxygen and carbonic anhydride are found to be present, the proportion of seven different gases will remain to be ascertained. The following method may be adopted for their quantitative determination:—

1. *Carbonic anhydride.*—A volume of the gas is confined over mercury, and its bulk is measured, with due attention to temperature and pressure. A piece of potassic hydrate which has been melted upon the end of a long platinum wire, to serve as a handle, is introduced from below, through the mercury into the tube. Care must be taken that the wire does not project above the surface of the mercury into the trough, otherwise a slow process of diffusion will occur between the gas in the tube and the outer air. After two or three hours the

potassic hydrate is withdrawn; the amount of the absorption indicates the proportion of carbonic anhydride which was present.

2. *Ethylene, Acetylene, and their Homologues.*—These gases are absorbed by introducing another ball, consisting of porous coke moistened with fuming sulphuric acid. It is necessary, however, before reading off the volume of the gas, to introduce a ball of potassic hydrate a second time, in order to withdraw the vapour of sulphuric anhydride, which possesses sufficient tension to introduce a serious error by dilating the bulk of the gas unless it be completely removed. The total amount of absorption will indicate the proportion of ethylene, together with the vapours of condensible hydrocarbons.

3. *Oxygen.*—This gas is determined in a similar manner, by employing a ball of moist phosphorus, which must be left in the gas for twenty-four hours; the fresh diminution in bulk, shows the proportion of oxygen. A ball of coke moistened with a concentrated solution of potassic hydrate and pyrogallic acid may be employed for the same purpose: the absorption in this case is much more rapid.*

4. *Carbonic Oxide.*—The accurate separation of carbonic oxide from the other gases is not easily effected. The gas may be divided into two portions, one of which is to be carefully measured as it stands over mercury; a small quantity of a solution of cuprous chloride in hydrochloric acid is next added by means of a syringe, and the mixture is briskly agitated; the gas is then withdrawn by means of the gas pipette (shown in fig. 305), and transferred by its means to a second graduated tube, also standing over mercury; into this tube a ball of potassic hydrate on the end of a platinum wire is introduced, for the purpose of absorbing the vapours of hydrochloric acid with which the gas is saturated; its bulk may then be read off, and the amount of carbonic oxide will be known by the decrease in volume which it has experienced.

The absorption of gases by liquid reagents is much more rapid than when moistened balls are employed, and provided that only very small volumes of liquid are used, the results are equally accurate. Carbonic anhydride may be thus absorbed by means of a concentrated solution of potassic hydrate, one or two drops of which will suffice; and oxygen may be withdrawn by a concentrated solution of pyrogallic acid and potassic hydrate.

5. *Nitrogen, Carbonic Oxide, Methane, and Hydrogen.*—The determination of the carbonic oxide, however, may be effected along with the methane and hydrogen without having recourse to absorption. Let a portion of the gas in which the carbonic oxide is still present be now transferred to a siphon eudiometer (fig. 287), and let its bulk, V, be accurately measured; then add about twice its volume of oxygen, and measure the gas a second time; let this bulk be V_1; $V_1 - V$ will give the volume of oxygen which has been added. Let V_2 be the bulk of the gas after the mixture has been exploded by the transmission of the electric spark: $V_1 - V_2$ indicates the diminution in bulk which it has experienced: call this a. Then inject a small quantity of a strong solution of potassic hydrate, and again note the volume, V_3. The absorption, $V_2 - V_3$, will be due to the quantity of carbonic anhydride which has been formed: call this b. The remaining gas, V_3, consists of oxygen in excess, and nitrogen. The quantity of oxygen in excess is ascertained by mixing the residual gas with about twice its bulk of hydrogen, and causing the electric

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* The use of pellets of appropriate materials may be extended to other gases: for example—*Sulphurous anhydride* may be absorbed by using a ball of moistened peroxide of manganese, or of peroxide of lead; and *hydrochloric acid* is rapidly absorbed by a ball consisting of crystallized hydric disodic phosphate.

spark to pass a second time. Let the volume of the mixture before firing be V_4, and let V_5 be the bulk after firing: $V_4 - V_5$ will represent the amount of condensation; and one-third of this, $\frac{V_4 - V_5}{3}$, will be due to the excess of oxygen. On deducting this from the residue, V_3, the difference gives the volume of nitrogen, n; $V_3 - \frac{V_4 - V_5}{3} = n$. The difference between the amount of the oxygen thus found to be in excess, and that originally introduced, will of course represent the quantity of oxygen consumed: call this c: thus $V_1 - V - \frac{V_4 - V_5}{3} = c$.

Assuming that the temperature of the gas has not varied in the course of the experiment, which may be insured by due precautions, we have now all the data for calculating the proportions of methane, of hydrogen, and of carbonic oxide, which are present in the mixture.

Let x represent the quantity of methane; this gas requires twice its own volume of oxygen for complete combustion, and furnishes its own volume of carbonic anhydride, which requires for its formation an equal volume of oxygen, or half the amount consumed; whilst the other half of the oxygen is required by the hydrogen which is condensed in the form of water; $2x$ will consequently represent the diminution in bulk of oxygen which occurs on detonation, due to the amount of carburetted hydrogen which is present.

Again, when hydrogen is converted into water, it requires half its bulk of oxygen, and both are condensed entirely. If y represent the bulk of the hydrogen, $\frac{3y}{2}$ will be the diminution in bulk of the mixed gases on detonation, which is occasioned by the hydrogen in the mixture.

Let z represent the volume of carbonic oxide present; carbonic oxide for its conversion into carbonic anhydride requires half its bulk of oxygen, the carbonic anhydride produced occupying the same bulk as the carbonic oxide. $\frac{z}{2}$ will therefore indicate the condensation which occurs on firing the mixture owing to the carbonic oxide present.

The total condensation in bulk, a, which occurs on firing a mixture of methane, hydrogen, and carbonic oxide, will consequently admit of being thus represented:

$$(1) \qquad a = 2x + \frac{3y}{2} + \frac{z}{2}.$$

Further, the quantity of the carbonic anhydride, b, formed by the detonation, is composed of a volume of carbonic anhydride equal in bulk to the methane and a volume equal to that of the carbonic oxide, so that the total quantity of carbonic anhydride may be thus indicated:

$$(2) \qquad b = x + z.$$

And lastly, the oxygen consumed, c, will be composed of the following quantities: by methane, twice its bulk, $2x$; by hydrogen, half its bulk, $\frac{y}{2}$; and by carbonic oxide, half its bulk, $\frac{z}{2}$; or the total quantity of oxygen consumed will be the following:

$$(3) \qquad c = 2x + \frac{y}{2} + \frac{z}{2}.$$

From these three equations the value of x, y, z are determined:

$$x = c - \frac{a+b}{3};$$
$$y = a - c;$$
$$z = \frac{a+4b}{3} - c.$$

Minute directions for the analysis of various gaseous mixtures are given by Regnault in the fourth volume of his *Cours Elémentaire de Chimie*, which contains a description of a form of eudiometer well adapted for accurate experiments; this eudiometer has been advantageously modified by Frankland and Ward (*Journ. Chem. Soc.* vi. 197). Bunsen has also introduced very important improvements into the manipulation and apparatus required for the analysis of gases, which are fully detailed in his *Gasometry*, translated by Roscoe (*see* also the article on Eudiometry, in Liebig and Poggendorff's *Handwörterbuch der Chemie*, vol. ii.); and the modes of manipulation have been still further simplified by Williamson and Russell. (*See* also Watt's *Dictionary*, i. 268, *Supplement*, p. 140, and Sutton's *Volumetric Analysis*, 2nd Edition, p. 300.)

(1050) *Calculation of Analyses.*—We will suppose the analysis brought to a successful issue, and the percentage of each element it contains calculated. It is evident that the information derived from this source is but scanty; for it furnishes no idea either of the simplest formula of the organic body, or of the relations of the body to the substances concerned in its production, or obtainable from it by its decomposition. The first thing is to ascertain the empirical formula of the compound, which can be easily done in the following manner. Suppose, to take a simple example, the results of the analysis have given 68·67 per cent. of carbon, 4·95 of hydrogen, and 26·38 of oxygen. If we divide the percentage of carbon by its atomic weight, 12, that of the hydrogen by 1, and the oxygen by 16, we obtain the numbers 5·723, 4·95, and 1·649 representing the atomic proportions of carbon, hydrogen, and oxygen respectively in the substance, so that its formula would be $C_{5·723}\ H_{4·95}\ O_{1·649}$. As, however, all definite compounds have formulæ with whole numbers, it becomes necessary to find approximately three whole numbers which bear the same relation to one another as these three fractions. The most convenient way of doing this is as follows:—Assume the oxygen to be 60, then the carbon and hydrogen will be found by the following proportions:

For the carbon	1·649	:	5·723	: :	60 : x
For the hydrogen	1·649	:	4·95	: :	60 : y

Here $x=208·2$ and $y=180·1$. Disregarding the decimals the formula may therefore be written $C_{208}\ H_{180}\ O_{60}$.

There are comparatively few substances which contain more than six atoms of oxygen, or O_6, and the number 60 was chosen for the oxygen as it is divisible by all the whole numbers less than six. Consequently, having assumed the oxygen as O_{60} and calculated the formula accordingly,—in this case $C_{208}\ H_{180}\ O_{60}$—we can readily find the empirical formula by inspection. It is here evident that the substance contains O_2, and dividing by 30 we obtain, approximately, the formula $C_7H_6O_2$, the carbon being as might be expected, a little lower than that required for C_7. On calculating the percentage of the formula $C_7H_6O_2$, *benzoic acid*, we can then compare it with the results of the analysis :

		Calculated.		Found.
$C_7=84$	...	68·85	...	68·67
$H_6=6$	...	4·92	...	4·95
$O_2=32$	...	26·23	...	26·38
122		100·00		100·00

The same principle is employed in calculating the empirical formula of more complex substances containing other elements in addition, such as nitrogen, chlorine, and sulphur.

§ III. MOLECULAR FORMULÆ.

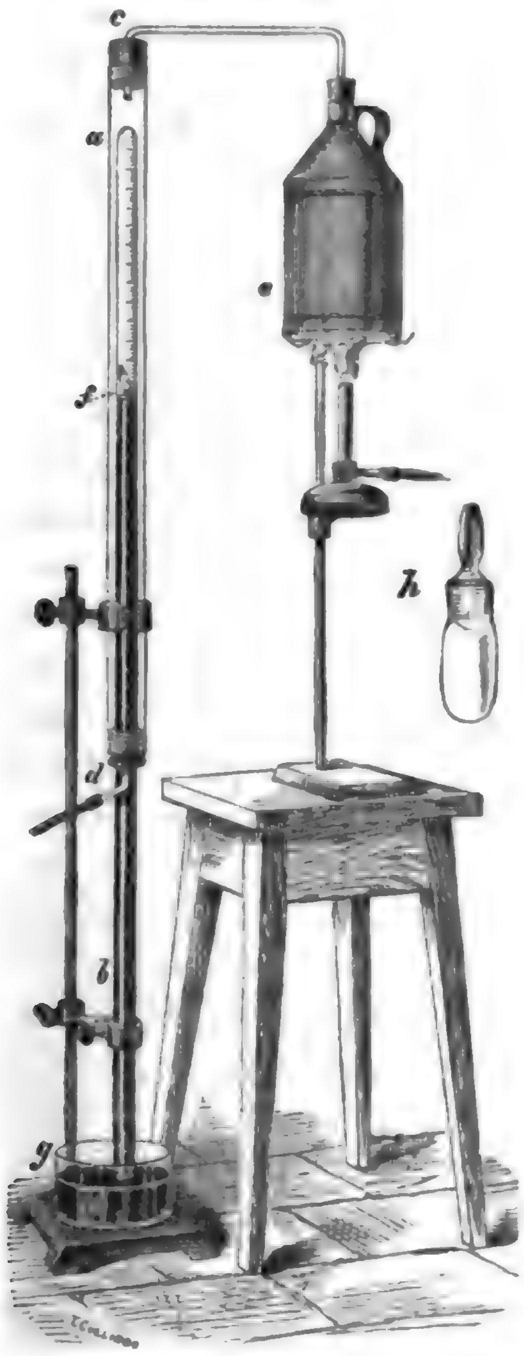
(1051) The empirical formula thus deduced is merely the simplest expression of the result of analysis in terms of the atomic weight of the elements contained in the compound analysed. It expresses the ratios in which the atoms are combined, but it does not afford any information as to the number of atoms of the various elements contained in a molecule of the compound. The molecular formula, however, is always either identical with, or some simple multiple of, the empirical formula.

The only method by which we are enabled to ascertain the molecular formula of a body with any certainty, is to determine its vapour density, or specific gravity in the gaseous state.

(1052) *Hofmann's Method for Vapour Densities.*—Of the two methods employed for this purpose which have been already described (Part I. p. 284) one is known as that of Dumas, and the other as Gay-Lussac's. A modification of the latter has recently been introduced by Hofmann which possesses many advantages and is available for determinations of all compounds whose boiling points are below 250° (482° F.) and which do not attack mercury.

The apparatus which is represented in fig. 389, consists of a graduated tube *ab* about 1 metre long, and 15 to 20 millims. wide, which is filled with dry mercury, and then inverted with the open end in the vessel *g*, also containing mercury. The upper portion of the laboratory tube *ab*, is surrounded by a wide glass tube *cd*, so that a current of the vapour of some liquid of constant boiling point, such as alcohol, water, or aniline, can be passed through the annular space between the two tubes. A small stoppered flask *h*, similar to that shown in the figure, but somewhat smaller, is completely filled with the substance under examination, the weight W of which must be ascertained. The flask and its contents is then carefully introduced into the laboratory tube *ab*, and on rising into the vacuum in the upper part, the stopper generally comes out of itself. A current of the vapour from the vessel *e* is now sent through the tube *cd*, the lower end of which is connected with a suitable condensing apparatus at *d*. This converts the liquid in the small flask at *f*, into vapour which soon attains a constant temperature, whilst the mercury column gradually sinks. As soon as this becomes stationary the volume in cubic centimetres V, of the vapour in the upper part of the tube is observed, together with the atmospheric pressure P, from a barometric reading, and also the height H, of the mercury column

Fig. 389.



fg, which must be corrected for the temperature of the heated portion of the column and also for the tension of the mercury vapour corresponding to the temperature, *t*.

The weight of an equal volume of hydrogen, V, under similar circumstances is:

$$0·0000895, V. \frac{P-H}{(1+0·00367\,t)\,760}$$

and the vapour density, D, of the substance is therefore given by the equation:

$$D = \frac{W(1+0·00367\,t)\,760}{0·0000895.\,V(P-H)}$$

As the vapour density is here determined under diminished pressure, the temperature required to obtain an accurate result is considerably lowered, and consequently unstable compounds are much less likely to undergo decomposition.

(1053) All bodies in the aëriform condition, whether simple or compound, if compared at equal temperatures, increase by an equal fraction of their volume for equal increments of temperature; in other words, they have the same coefficient of dilatation when heated. In like manner equal volumes of all gases and vapours undergo equal amounts of compression, for equal increments of pressure, if the comparison be made under similar circumstances. It appears, therefore, that the elastic force of all gases, whether simple or compound, is sensibly equal and uniform; hence it has been concluded that under similar circumstances of temperature and pressure equal volumes of all gases and vapours contain an equal number of molecules. This hypothesis of the constitution of gases we owe to Avogadro and Ampère.

Assuming then that equal volumes of gases contain an equal number of their constituent molecules, it follows that the relative weights of these molecules must be the same as the relative weights of the equal gas volumes. Adopting as a standard the hydrogen molecule weighing 2, we may therefore say that the weight of the molecule of any gas is expressed by a number equal to twice its specific gravity referred to hydrogen, so that in order to ascertain the molecular weight of any substance in the gaseous state, we have simply to determine its specific gravity with reference to hydrogen, and to double the number thus obtained. The volume V, which a given weight of the compound occupies when converted into vapour at the temperature *t*, and under the pressure P, being ascertained by experiment, the required vapour density D, of the compound referred to hydrogen as unity is found by dividing this volume by the weight of an equal volume P, of hydrogen also at the temperature t, and pressure V_1:

$$D = \frac{V}{V_1}$$

If the density of the vapour be referred to air as unity, the density referred to hydrogen as unity is at once given on dividing by ·06926, the specific gravity of hydrogen referred to air.

On the other hand, the density corresponding to any particular formula is found by dividing the sum of the atomic weights of the elements composing the compound represented by the formula in question by 2. Thus the empirical formula of turpentine as determined by analysis is C_5H_8, the density corresponding to which is

$$\frac{12 \times 5 + 1 \times 8}{2} = \frac{68}{2} = 34,$$

but the number obtained on determining the vapour density of that substance is approximately* 68; hence the molecular formula of turpentine is twice C_5H_8, or $C_{10}H_{16}$. Similarly, analysis shows that the empirical formula of benzene is CH, the density corresponding to which is

$$\frac{12 + 1}{2} = \frac{13}{2} = 6{\cdot}5.$$

The vapour density, however, is determined to be approximately 39; it becomes necessary, therefore, to multiply the empirical formula CH by 6 in order to obtain the molecular formula of benzene. This gives C_6H_6 as the formula corresponding to the density 39. Again, the empirical formula of ether as determined by analysis is $C_4H_{10}O$, whence

$$D = \frac{12 \times 4 + 1 \times 10 + 16}{2} = 37;$$

the experimental determination of its vapour density gives as result the number 37·13. In this case, therefore, the empirical is shown to coincide with the molecular formula.

(1054) It is not always possible to fix the molecular formula of a compound by determining its vapour density, as many substances cannot be volatilized without undergoing decomposition. In such cases the molecular formula can only be ascertained by a study of the chemical and physical properties of the compound, and a careful investigation of a number of its derivatives.

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* Owing to unavoidable experimental errors, the numbers obtained are never exact.

The molecular formula may often be approximately determined, or rather, to speak exactly, an estimate obtained in favour of the adoption of the empirical formula deduced from the analysis, or of some particular multiple thereof, if the compound possesses acid or basic properties, *i.e.*, if it be capable of yielding salts or combining with acids. For example, the simplest formula deducible from the analysis of acetic acid is CH_2O; is acetic acid most probably represented by this formula, or by $C_2H_4O_2$, $C_3H_6O_3$, &c., or, in other words, is the molecular weight 30, 60, or 90? Information on this point is afforded by the analysis of the silver salt prepared from the acid.

It is found that 4·873 grains of silver acetate yield a residue of 3·149 grains of metallic silver on ignition. If then 3·149 of silver are contained in 4·873 of silver acetate, how much silver acetate will contain 108 (1 atom) of silver? By the proportion:

$$3{\cdot}149 : 108 : : 4{\cdot}873 : x \ (=167),$$

we find 167 for the molecular weight of the silver salt, supposing the acid to be monobasic, and in order to ascertain the molecular weight of the acid, we must deduct from this 108—the number of parts of silver it contains, and add 1—the number of parts of hydrogen replaced by 108 of silver, and we thus obtain as result the number 60. It is thus proved that the molecular formula of acetic acid is not CH_2O, but that it is either $C_2H_4O_2$ or some multiple thereof. What the molecular formula really is can only be determined by ascertaining the vapour density. This is found on trial to be approximately 30, and the molecular formula is thus finally fixed as being $C_2H_4O_2$.

In a similar manner the potassium, sodium, barium, lead, or other salts may be employed. In the case of basic substances, either the amount of substance associated with one or more molecules of an acid is determined by analysis, *e.g.* the hydrochloric acid in the hydrochloride of the base, or the amount of platinum contained in the double salts which many of the hydrochlorides of bases form with platinic chloride.

(1055) *Polymeric, metameric, and isomeric compounds.*—Compounds which have the same percentage composition, and therefore the *same empirical formula*, but which are represented by *different molecular formulæ*, are said to be *polymeric*. Thus, cyanic acid and cyanuric acid are called polymeric, as although both have the same empirical formula, CNOH, the molecular formula of the former is CNOH, whilst that of the latter is $C_3N_3O_3H_3$. In a similar manner, cyanic chloride, CNCl, and cyanuric chloride, $C_3N_3Cl_3$, are polymeric, and also aldehyde, C_2H_4O, and paraldehyde, $C_6H_{12}O_3$.

Bodies possessing the same percentage composition, and also the same molecular formula, are considered to be either *metameric* or *isomeric*, according to the relation which they bear to one another in their physical properties and chemical behaviour. Thus, they are said to be metameric when there is a marked difference in their physical properties, and in their behaviour under the influence of chemical reagents; whilst isomeric bodies are those which may be shown to be members of the same series, either by their method of formation, or by the analogous changes which they undergo when submitted to the action of various reagents. Propionic aldehyde and acetone, for instance, are considered to be metameric, as when treated with oxidizing agents the former is converted into propionic acid:

$$\underset{\text{Propionic aldehyde.}}{2\,C_3H_4O} + O_2 = \underset{\text{Propionic acid.}}{2\,C_3H_4O_2};$$

whilst the latter yields formic and acetic acid:

$$\underset{\text{Acetone.}}{C_3H_4O} + O_2 + OH_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Formic acid.}}{CH_2O_2}.$$

On the contrary, the three dimethylbenzenes, known as orthoxylene, metaxylene, and paraxylene, having the molecular formula, $C_8H_{10} = C_6H_4(CH_3)_2$, are called isomeric compounds, for they can be obtained from benzene by the displacement of two of the hydrogen atoms by the methyl group, CH_3, and when oxidized by dilute nitric acid they yield three corresponding methylbenzoic acids, $C_6H_4(CH_3).COOH$. Another hydrocarbon, C_8H_{10}, is known, which is metameric with the three dimethylbenzenes; it is ethylbenzene, $C_6H_5.C_2H_5$, obtained by the displacement of one of the hydrogen atoms in benzene by the ethyl group, C_2H_5. When oxidized it is converted into benzoic acid, $C_6H_5.COOH$.

The term isomeric, however, is frequently employed in a more extended sense to signify compounds which have the same percentage composition, but which differ in chemical properties.

CHAPTER II.

§ I. *Quantivalence ;*—§ II. *Classification of Carbon Compounds ;*—§ III. *Theory of Compound Radicles.*

§ I. QUANTIVALENCE.

(1056) OBSERVATION has shown that each elementary substance has a tendency to unite with the other elements in a particular manner, and the special peculiarities of these combinations have rendered it necessary to arrange the elements in six principal groups (see also Part I., p. 35) of *monads, dyads, triads, tetrads, pentads,* and *hexads,* according as they are equivalent in combining or replacing power to one, two, three, four, five, or six monad atoms of hydrogen. The particular class of the element or radicle may, when needful, be pointed out as proposed by Odling by affixing the marks $(^{\prime})$ $(^{\prime\prime})$ $(^{\prime\prime\prime})$ $(^{\text{IV}})$ $(^{\text{V}})$ $(^{\text{VI}})$ to indicate its monad, dyad, triad, tetrad, pentad, or hexad character.

All the members of the same group exhibit a certain similarity, for when any one of them enters into combination with another element, *A,* the compound so formed is usually similar in composition to the compounds which the other members of the group form with the same element, *A.*

(1057) A distinction has already been drawn (p. 29, Part I.) between, 1. the *Atom,* which is the smallest chemically indivisible particle of each element which can exist in a *compound* united with other particles either of the same or of different kinds of matter, but which is not known in a separate form ; and 2, the *Molecule,* or the smallest quantity of any elementary substance which is capable of existing in a *separate form.* H, for instance, indicates the *atom* of hydrogen, whilst $\left.\begin{matrix}H\\H\end{matrix}\right\}$ or H_2, represents its *molecule.*

The molecule of a compound must, it is obvious, consist of at least two atoms, since it cannot consist of less than one atom of at least two different kinds of matter; and in like manner it is probable that the molecules of most of the bodies hitherto described as isolated elements are compounds of the element with itself. If this view be correct, it must happen that when such bodies unite with other so-called elements of the same group, the act of combination is attended by double decomposition, and not by direct union.

When, for example, hydrogen and chlorine unite to form hydrochloric acid, the change should be thus represented :

$$H_2 + Cl_2 = HCl + HCl;$$

the equation indicating that one of the atoms in the molecule of hydrogen changes place with one of the atoms of chlorine in the molecule of chlorine; and the result is, the formation of *two* molecules of hydrochloric acid.*

In further justification of this view, it may be stated as a uniform result of observation, that in all the reactions in which chlorine gas is concerned, not one is known in which less than two atoms of chlorine is required. Take, for example, the successive steps of the action of chlorine upon ethylenic chloride:

$$\begin{aligned} C_2H_4Cl_2 + Cl_2 &= C_2H_3Cl_3 + HCl \\ C_2H_3Cl_3 + Cl_2 &= C_2H_2Cl_4 + HCl \\ C_2H_2Cl_4 + Cl_2 &= C_2H\,Cl_5 + HCl \\ C_2H\,Cl_5 + Cl_2 &= C_2Cl_6 \;+\; HCl \end{aligned}$$

As this is true in all other cases, it has been concluded that the molecule of chlorine, that is the smallest particle which can exist in the free state, must contain two atoms of chlorine.

It has also been observed that at least two atoms of bromine, or of iodine, must be present in every reaction in which they take part; and the same is true of hydrogen and of all the metals which correspond to hydrogen in atomic character. Many compound substances, indeed, may be looked upon as intermediate between the elements or the radicles which enter into their formation; as for instance:

1. Hydrogen	HH	Sodium	NaNa
2. Hydrochloric acid . .	HCl	Sodic iodide	NaI
3. Chlorine	ClCl	Iodine	I I

In like manner the alkaline hydrates and such bodies as hypochlorous acid may be regarded as compounds intermediate between water and the anhydrous oxides:

1. Water	HHO	Water	HHO
2. Potassic hydrate . . .	KHO	Hypochlorous acid . . .	HClO
3. Potassic oxide . . .	KKO	Hypochlorous anhydride .	ClClO

So also hydric potassic sulphide is intermediate between sulphuretted hydrogen and dipotassic sulphide.

It is frequently the case that the most probable inference respecting the magnitude of the molecule of a body, the vapour density of which cannot be ascertained, is founded upon the formation of such intermediate compounds. For example, it is inferred that the molecule of ethylic (or ordinary) ether cannot be less than $C_4H_{10}O$, because of the existence of methyl ethyl ether, which is a compound intermediate between ethyl ether and methyl ether:

$$1.\quad \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O; \qquad 2.\quad \left.\begin{matrix} C\,H_3 \\ C_2H_5 \end{matrix}\right\} O; \qquad 3.\quad \left.\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\} O.$$

Ethyl ether. Methyl ethyl ether. Methyl ether.

In this case the supposition is confirmed by the vapour density of the compounds which correspond to these formulæ.

It must not, however, be supposed that there is no such thing as direct combination between two bodies: the molecules of compounds frequently exhibit the power of uniting in this manner, in which case the number of molecules of the new body is smaller than the sum of those of its components: in other words, condensation occurs. When, for instance, 1 molecule of carbonic oxide and 1 of chlorine unite, they form 1 molecule of carbonic oxychloride; $CO + Cl_2$, yielding $COCl_2$. One molecule of mercury and 1 of chlorine yield 1 of mercuric chloride; $Hg + Cl_2 = HgCl_2$; and 1 molecule of ethylene and 1 of bromine yield 1 of ethylenic dibromide; $C_2H_4 + Br_2 = C_2H_4Br_2$. In like manner, ammonia and hydrochloric acid combine directly; $H_3N + HCl$ becoming H_4NCl. Nitric oxide with oxygen forms nitrogen dioxide; $NO + O$ becoming NO_2.

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* Sir B. Brodie explains this phenomenon by a different hypothesis, for the development of which the reader is referred to his paper, "On the Calculus of Chemical Operations" (*Phil. Trans.* 1866, 781).

(1058) In order to explain the combination of the elements with one another, each atom of every element is supposed to have a certain definite number of centres of attraction, or *bonds* as they have been called by Frankland, by which, and by which alone, it unites with other elements. To aid in giving precision to our ideas, these bonds or points of attachment may be represented graphically; and this has been done in various ways, the most convenient, perhaps, being to write the symbol of the element with as many lines attached to it as the element has bonds.

The atom of a monad, such for example as hydrogen, is assumed to have but a single such bond, which is indicated by a single line, thus, H—; the same is supposed to be true of each monad, the atom of chlorine being Cl—. In the *molecule* of hydrogen H_2 as it exists in the gas, the attraction of each atom is saturated by that of its fellow, thus, H—H; and the same is assumed to hold good in the molecule of other elementary monads, such as gaseous chlorine, Cl—Cl. When combination occurs between two monads, they can only unite in one proportion, and a single molecule of one element, by reacting on a single molecule of the other element, gives rise to two molecules of the compound: H—H + Cl—Cl becoming H—Cl + H—Cl; hence also, no monad element or radicle has the power of effecting the union of two or more monad elements or radicles into one polyatomic molecule.*

Each atom of a dyad is supposed to have two points of union. Consequently, it may unite with each of two atoms of the same monad, or with one atom of two different monads, or it may form a more complex group by uniting with other dyads in various ways, or it may even cause the union of several compound radicles of more or less simple constitution into one group or compound molecule.

One atom of oxygen, for instance, may unite with two atoms of hydrogen, with two of chlorine, or with one of chlorine and one of hydrogen; or it may unite with a second atom of oxygen, or with an atom of some other dyad, such as zinc; as for instance:

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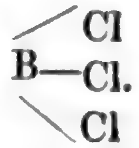
* A molecule which consists of a single atom is called a monatomic molecule, if it consists of two atoms diatomic, and if of three triatomic. Similarly, we may speak of monatomic, diatomic, triatomic radicles, and so on, according to the number of atoms they contain.

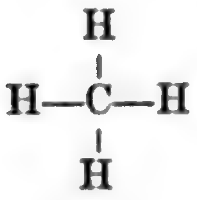
$H—O—H$; $Cl—O—Cl$; $H—O—Cl$; $O=O$; $O=Zn$.

Water. Hypochlorous anhydride. Hypochlorous acid. Oxygen gas. Zinc oxide.

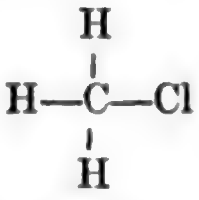
In this case the different elements are represented as being so united that both the bonds of the dyad are saturated. But, on the other hand, two atoms of the same or of different dyads may be supposed to be so united that only one of the two points of union is saturated, leaving therefore two other bonds unsaturated and ready to enter into combination to that extent with some other element or compound. Such a union would give rise to a dyad diatomic radicle with two unsaturated bonds, such as —O—O—, —S—S—, &c.

In the case of a triad like boron or gold there are supposed to be three such centres of attraction, boric chloride, for example, being represented by the formula,  Combination with a dyad such as oxygen, as in boric anhydride, B_2O_3, may be represented thus: $O=B-O-B=O$.

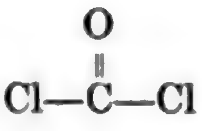
The relation of the tetrad elements, of which carbon is by far the most important, are somewhat more complex, and hence the vast variety of combinations which we meet with among the compounds of carbon. Methane or marsh gas, CH_4, may be taken as the simplest instance of a saturated molecule containing carbon. It will also afford a good illustration of the effect of the removal of hydrogen and the substitution for it of a monad such as chlorine in monochloromethane or methylic chloride, CH_3Cl; a monad and a dyad as in carbonic oxychloride, $COCl_2$; or two dyads as oxygen in carbonic anhydride, CO_2, or sulphur in carbonic disulphide, CS_2:


$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

Methane.


$$\begin{array}{c} H \\ | \\ H—C—Cl \\ | \\ H \end{array}$$

Monochloromethane.


$$\begin{array}{c} O \\ \| \\ Cl—C—Cl \end{array}$$

Carbonic oxychloride.

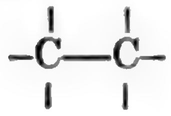
$O=C=O$

Carbonic anhydride.

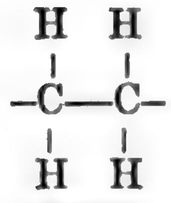
$S=C=S$

Carbonic disulphide.

When substances are formed, into the composition of which more than one atom of carbon enters, it is assumed that the atoms of carbon are riveted together by partial saturation. If the pair of atoms be united by single bonds, it is evident that the group C_2 will be hexad in power. Consequently, if ethylene or olefiant gas, C_2H_4, contains two atoms of carbon so united, it will furnish a radicle of dyad power; that is to say, as indeed is the fact, that it should show a readiness to unite with two atoms of some monad, such as chlorine, when it forms ethylenic chloride $C_2H_4Cl_2$. Indeed we may regard most of the dicarbon compounds as formed from 2 atoms of carbon retaining a hexad power, thus:

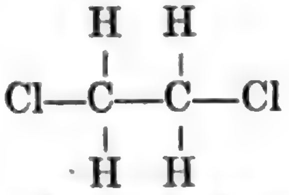


$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$



$-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-$

Ethylene.



$Cl-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Cl$

Ethylenic Chloride.*

Ethane or ethylic hydride	$C_2^{vi}H_6$
Monochlorethane or ethylic chloride .	$C_2^{vi}H_5Cl$
Hexachlorethane	$C_2^{vi}Cl_6$
Aldehyd	$C_2^{vi}H_4O$
Chloral	$C_2^{vi}HCl_3O$
Acetonitrile	$C_2^{vi}N'''H_3$
Cyanogen gas (*Dicyanogen*)	$C_2^{vi}N'''_2$

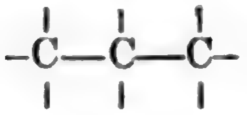
But it is quite possible that the two atoms of carbon may be united by two of their bonds, in which case a tetrad group would be the result; and in other instances the union may be by three out of the four bonds, leaving only two unsaturated points. In the last case, by their union with two atoms of a dyad, a molecule like acetylene, C_2H_2, would be the result. Compounds containing 3 atoms of carbon would thus, if united by single bonds, require 8 atoms of a monad to complete the molecule; with 4 atoms of carbon, 10 bonds would require saturation; with 5 atoms, 12 atoms of a monad would be needed; and generally, if n represent the number of atoms of carbon, the number of bonds in the molecule requiring saturation would be $2n+2$, as will be seen by inspecting the subjoined graphic formulæ:

$=C=C=$

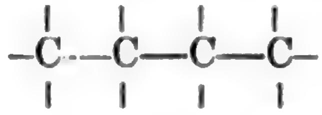
$-C\equiv C-$

$H-C\equiv C-H$

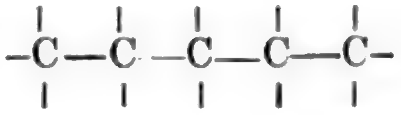
Acetylene.



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$;



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$;



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$

In strict correspondence with this is the fact that no compound of carbon and hydrogen is known in which the number of atoms of hydrogen exceeds this proportion.

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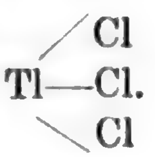
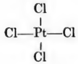
* It is scarcely necessary to remind the reader that the graphic illustrations employed to aid the conception are not intended in any way to represent the relative position of the atoms, but merely to show whether the compound is a saturated or an unsaturated group or molecule.

(1059) In the foregoing remarks no notice has been taken of the fact that the valency of an element appears to vary according to the nature of the element or elements with which it is associated. Thus, nitrogen, phosphorus, and arsenic, which in a large number of their compounds are triads—the compounds NH_3, PCl_3, PH_3, $AsCl_3$ may be cited as examples—are also capable of entering into combination as pentads; for instance, to form such well known compounds as PCl_5, NH_4Cl, etc. Similarly, iodine which appears to be a monad in such bodies as KI is a triad in ICl_3; tin in certain of its compounds is apparently a dyad, but in others a tetrad; and sulphur appears even to be capable of playing the part of a dyad, tetrad, or hexad. On this account, the elements cannot be strictly classified in groups according to their valency. It has also been observed that, in a number of instances, the same element apparently enters into combination either as a dyad and triad, or as a dyad, triad, and tetrad, etc. There is reason to believe, however, that the atom of those elements whose valency is denoted by an even number (so-called *artiads*) cannot enter into combination with an odd number of atoms of a monad, or the equivalent amount of a polyad element; and that the atom of those elements whose valency is denoted by an odd number (*perissads*) cannot enter into combination with an even number of atoms of a monad, or the equivalent amount of a polyad element. The variation in valency which thus apparently takes place, and the fact that the same element may seemingly act as an artiad and perissad is explained in various ways :—

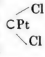
First, taking Naquet's rule, it is supposed that the highest known compound determines the valency of an element, and that in each of the lower compounds two of the bonds neutralize each other (Frankland). In thallious chloride TlCl for instance, CTl—Cl, two of the three bonds of thallium neutralize each other, whilst in the rarer instances, as when thallic chloride $TlCl_3$ is formed, each of the three bonds is saturated by chlorine. In such cases of partial saturation of the atom as in thallious chloride, the other bonds in each molecule neutralize each other *in pairs*; and hence the tendency of all the elements to preserve their mode of combination, either always with an odd number of atoms of a monad, or else always with an even number. Every element tends to form one particular class of compounds, which are more stable than any other series into the formation of which it enters.



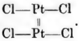
For example, the stable thallium compounds are generally those in which the metal appears to act the part of a monad, not of a triad; corresponding, that is, to $TlCl$, not to $TlCl_3$. With gold, on the contrary, though compounds like aurous chloride, $AuCl$, may be obtained, the most stable series is that in which the triad character of the metal is distinctly shown, as in the trichloride, $AuCl_3$.



$$\begin{array}{c} Cl \\ | \\ Cl—Pt—Cl \\ | \\ Cl \end{array}$$



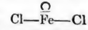
Again, in the group of tetrads, although platinum generally forms compounds on the type of platinic chloride, $PtCl_4$, it occasionally forms them on that of platinous chloride, $PtCl_2$, in which it may be supposed that the two unsaturated bonds are neutralized by reacting one against the other. Such a mode of representing the formation of the inferior compounds seems to be suited especially to gaseous compounds like carbonic oxide $CC{=}O$, as compared with carbonic anhydride $O{=}C{=}O$; where the specific gravity of the gas defines distinctly the molecule of each.

A second explanation of the method of combination in multiple proportion, which is admissible in certain cases, is the following:—It is supposed that in the lower compounds, such as the aurous and platinous groups, two atoms of the element have partially neutralized each other; for instance, aurous chloride, Au_2Cl_2, may be represented as $Cl—Au{=}Au—Cl$, and platinous chloride, Pt_2Cl_4, as  $\begin{array}{c} Cl—Pt—Cl \\ \| \\ Cl—Pt—Cl \end{array}$. On this view it becomes necessary to double the formula ordinarily employed to represent the molecule.

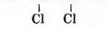
Upon either hypothesis a reasonable explanation may be given of the remarkable cases presented where the same element, like iron, seems to combine with the monads in proportions represented by both odd and even numbers.

It is, however, necessary to suppose that in such cases as those of iron and the other metals allied to it, viz., cobalt, nickel, manganese, chromium, uranium, and aluminum, they should be viewed as tetrads. If this be granted, the ferrous compounds, such as ferrous chloride, may be represented either as $FeCl_2$, where two of the bonds neutralize each other; or as Fe_2Cl_4, where the two atoms of iron are represented as united by two points of attraction. In *ferric* compounds (like ferri

which we know from th

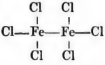


$$Cl—\overset{\frown}{Fe}—Cl$$



$$\begin{array}{l} Cl—Fe{=}Fe—Cl \\ \quad\ \ | \qquad\ \ | \\ \quad\ Cl \qquad Cl \end{array}$$

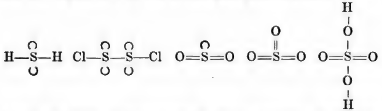
vapour that the molecule cannot be less than that indicated by the formula $Fe_2{}^{vi}Cl_6$, each atom of iron in the molecule must be united to its fellow by a single bond only, as represented in the diagram below.



$$\begin{array}{ccc} & Cl & Cl \\ & | & | \\ Cl- & Fe - & Fe-Cl \\ & | & | \\ & Cl & Cl \end{array}$$

A similar plan would be supposed to prevail in the constitution of the molecule of aluminic chloride, the density of which corresponds with the formula $Al_2{}^{vi}Cl_6$, as well as in the case of the analogous body, chromic chloride.

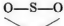
According to Frankland's view sulphur is a hexad, and in the compounds in which it apparently plays the part of a dyad or tetrad one or two pairs respectively of the bonds saturate each other. The compounds SH_2, S_2Cl_2, SO_2, SO_3, SO_4H_2 are on this view represented by the following graphic formulæ :—

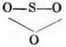


$$H-\overset{\frown}{\underset{\smile}{S}}-H \quad Cl-\overset{\frown}{\underset{\smile}{S}}-\overset{\frown}{\underset{\smile}{S}}-Cl \quad O=\overset{\frown}{S}=O \quad O=\overset{\overset{O}{\|}}{S}=O \quad O=\overset{\overset{\overset{H}{|}}{\overset{O}{|}}}{\underset{\underset{\underset{H}{|}}{\underset{O}{|}}}{S}}=O$$

Kekulé and some other chemists maintain, however, that sulphur is uniformly a dyad and represent the above compounds by the following formulæ :—

H—S—H Cl—S—S—Cl





H—O—O—S—O—O—H

In a similar manner different views are held with regard to the valency of several of the other elements.

§ II. Classification of Carbon Compounds.

(1060) One of the most characteristic differences between carbon and the other elements is that it is capable of uniting with hydrogen in various definite proportions to form a great variety of compounds termed hydrocarbons. These are of great interest, especially from a theoretical point of view, since all carbon compounds may be considered as derived from them by substitution, either directly or indirectly. It is for this reason that many [illegible] define [illegible]ic chemistry as the chemistry of the hy[illegible] [illegible]tives.

(1061) I. HYDROCARBONS.—Carbon being a tetrad element, its atom is capable of uniting with at most *four atoms* of hydrogen; thus, the simplest known hydrocarbon, containing relatively the smallest amount of carbon in proportion to the hydrogen, is *methane* or marsh gas, which has the composition expressed by the formula CH_4.

Methane is the first or lowest term of a *series* of hydrocarbons of gradually increasing complexity, all of which consist of carbon and hydrogen associated in the same proportion as in methane—namely, that expressed by the *general formula*, C_nH_{2n+2}; n atoms of carbon being always associated with $2n+2$ atoms of hydrogen. In the following list the names and formulæ of the first ten members of the series are given:—

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Tetrane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$.

It will be observed that between each successive term in this series there is a constant difference of CH_2. Bodies which are thus related to one another are said to be *homologous* (from ʽομὸς, like; λόγος, a word), because a similar description is applicable to the different members of the series, since they are not only related in composition, but also resemble each other very closely in chemical behaviour. Substances belonging to the same homologous series, however, generally exhibit a certain *graduated* relation in physical properties, such as boiling-point, specific gravity, &c.

The hydrocarbons of the methane or marsh-gas series, C_nH_{2n+2}, are generically termed *paraffins*, after the well-known wax-like substance paraffin, which is principally a mixture of the higher and more complex members of the series. It is to be remarked that the paraffins are *saturated compounds*, that is, they cannot enter directly into combination; they are, however, capable of yielding derivatives by exchanging one or more atoms of hydrogen for the equivalent quantity of another element, or of one or more of the groups of elements, termed compound radicles.

It is possible to remove hydrogen from the paraffins by certain known methods, and thus convert them into *unsaturated* hydrocarbons, that is, hydrocarbons which are capable of uniting directly with some of the elements, notably the halogens. It is found, however, that it is not possible to obtain hydrocarbons derived from the paraffins by the removal of an *odd number* of hydrogen atoms; these compounds, in fact, do not appear to be capable of existing, since, in all reactions where their formation might be expected, we obtain a compound whose molecular formula is double that which would be assigned to such a hydrocarbon. Methane, for example, when treated in such a manner as to remove one atom of hydrogen from it, does not yield CH_3, but the hydrocarbon C_2H_6, which may be regarded as being formed by the union of CH_3 with CH_3. Whenever, in short, the hydrocarbons are so acted upon as to become converted by loss of hydrogen into hydrocarbons containing the same number of carbon atoms in the molecule, the number of hydrogen atoms eliminated is always 2, or some simple multiple of 2. From this it naturally follows that the number of hydrogen atoms in the new hydrocarbon is always divisible by two. A series of hydrocarbons in which the number of carbon atoms is the same, but which differ by H_2, are said to be *isologous*.

The following is a list of the isologous series of hydrocarbons of which up to the present time members have been obtained and investigated:—

C_nH_{2n+2} or Paraffin series of hydrocarbons.
C_nH_{2n} or Olefine „
C_nH_{2n-2} or Acetylene „
C_nH_{2n-4} or Terpene „
C_nH_{2n-6} or Benzene „
C_nH_{2n-8} or Cinnamene „
C_nH_{2n-10} or Acetenylbenzene „
C_nH_{2n-12} or Naphthalene „
C_nH_{2n-14} or Diphenyl „
C_nH_{2n-16} or Stilbene „
C_nH_{2n-18} or Anthracene „
C_nH_{2n-20} or Benzylnaphthalene „
C_nH_{2n-22} or Pyrene „
C_nH_{2n-24} or Chrysene „
C_nH_{2n-26} or Dinaphthyl „

C_nH_{2n-30} or Idrialene „
C_nH_{2n-32} or Tetraphenylethylene „

Several of these isologous series of hydrocarbons have only a single representative; others contain two or three homologues.

Few, however, are so well represented, or have been so thoroughly investigated as the paraffins, of which 16 homologous terms are at present known, besides several isomerides.

(1062) *Haloid-derivatives of the hydrocarbons.*—By the direct action of chlorine or bromine on the hydrocarbons, one or more atoms of hydrogen may be displaced by an equivalent quantity of the halogen; thus the action of chlorine on methane gives rise to mono-, di-, tri-, and finally tetra-chloromethane:

$$CH_4 \qquad CH_3Cl \qquad CH_2Cl_2 \qquad CHCl_3 \qquad CCl_4.$$

Similarly, by the action of bromine on benzene, C_6H_6, the following series of bromobenzenes is produced:

C_6H_5Br	Bromobenzene.
$C_6H_4Br_2$	Dibromobenzene.
$C_6H_3Br_3$	Tribromobenzene.
$C_6H_2Br_4$	Tetrabromobenzene.
C_6HBr_5	Pentabromobenzene.
C_6Br_6	Hexabromobenzene.

The hydrogen in the hydrocarbons may also be indirectly displaced by iodine.

These haloid derivatives are a most important class of compounds, inasmuch as they serve, in many cases, so to speak, as stepping stones from the hydrocarbons to other classes of bodies, such as the alcohols and acids; the mono-haloid derivatives of the paraffins being identical with the so-called haloid ethers: thus monochlorethane, C_2H_5Cl, and ethylic chloride are the same substance.

(1063) *Cyano-derivatives of the hydrocarbons.*—By the action of metallic cyanides on many of the haloid derivatives of the hydrocarbons, more particularly the iodo-derivatives, the corresponding cyano-derivatives are produced; thus iodethane when acted upon by argentic cyanide is converted into a cyanoethane:

$$C_2H_5I + AgCN = C_2H_5(CN) + AgI.$$

(1064) *Nitro-derivatives of the hydrocarbons.*—In some cases the direct action of concentrated nitric acid on the hydrocarbons effects the displacement of one or more atoms of hydrogen by the monad group NO_2, giving rise to nitro-compounds, thus:

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + OH_2.$$

$$\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + HNO_3 = \underset{\text{Dinitrobenzene.}}{C_6H_4(NO_2)_2} + OH_2.$$

As the hydrocarbons of the paraffin series and many others cannot be converted into nitro-derivatives by this means, other methods must be resorted to; thus the mononitro-paraffins may be prepared by the mutual action of the iodo-derivatives of the hydrocarbons and argentic nitrite:

$$\underset{\text{Iodethane.}}{C_2H_5I} + AgNO_2 = \underset{\text{Nitroethane.}}{C_2H_5.NO_2} + AgI$$

(1065) II. ALCOHOLS.—The alcohols may be regarded as the hydroxyl derivatives of the hydrocarbons—that is to say, as derived from the hydrocarbons by the substitution of one or more OH groups for the same number of hydrogen atoms. The alcohols are in all respects the analogues of the metallic hydrates, and may frequently be obtained from the haloid derivatives of the hydrocarbons by methods which are similar to those by which the metallic hydrates are formed from the metallic chlorides, &c. Thus we have, for example,

$C_2H_5.OH$ Ethylic hydrate (ordinary alcohol).	corresponding to	$NaOH$ Sodic hydrate.
$C_2H_4(OH)_2$ Ethylenic hydrate.	"	$Ca(OH)_2$ Calcic hydrate.
$C_3H_5(OH)_3$ Glyceric hydrate (glycerin).	"	$Bi(OH)_3$ Bismuthic hydrate.

The alcohols are appropriately termed *monohydric*, *dihydric*, *trihydric*, *&c.*, according to the number of semimolecules of hydroxyl, OH, which may be regarded as present; an alcohol containing one OH group being called a monohydric alcohol, if it contains two such groups dihydric, and so on. Each homologous series of hydrocarbons appears to be capable of yielding a corresponding homologous series of alcohols, but of the very large number which are theoretically possible, comparatively few are at present known. The monohydric alcohols derived from the paraffins are the most numerous and have received a greater share of attention than any others; the series includes several well-known substances, such as ordinary alcohol, wood spirit, and amylic alcohol (fusel oil). Glycerin again is a trihydric alcohol derived from the third term of the paraffin series of hydrocarbons, and mannite and dulcite, two bodies of vegetable origin, are hexahydric alcohols derived from the sixth term of the paraffin series, being intimately related to that most important group of substances, the sugars. Phenol, moreover, the so-called carbolic acid, is the monohydric alcohol of benzene, the first term of the C_nH_{2n-6} series of hydrocarbons.

(1066) *Thio-alcohols* or *mercaptans.*—These bear the same relation to the alcohols that the metallic sulphydrates bear to the metallic hydrates, as will be evident from the following examples:—

	Alcohols.		Thioalcohols.
$C_2H_5.OH$	Ethylic hydrate.	$C_2H_5.SH$	Ethylic sulphydrate.
$C_6H_5.OH$	Phenol.	$C_6H_5.SH$	Thiophenol.
$C_2H_4(OH)_2$	Ethylenic hydrate.	$C_2H_4(SH)_2$	Ethylenic sulphydrate.
$C_3H_5(OH)_3$	Glyceric hydrate.	$C_3H_5(SH)_3$	Glyceric sulphydrate.
	Metallic hydrates.		Metallic sulphydrates.
$NaOH$	Sodic hydrate.	$NaSH$	Sodic sulphydrate.
$Ca(OH)_2$	Calcic hydrate.	$Ca(SH)_2$	Calcic sulphydrate.

(1067) *Chlorhydrins, Bromhydrins, &c.* — Certain haloid derivatives of the hydrocarbons are converted by more or less prolonged heating with water into corresponding alcohols; trichloropropane, for example, may thus be converted into glycerin:

$$\underset{\text{Trichloropropane.}}{C_3H_5Cl_3} + 3OH_2 = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + 3HCl.$$

Many of the alcohols on the other hand when heated with the haloid acids in concentrated aqueous solution, undergo a change which is of the reverse order. Thus when glycerin is heated with hydrochloric acid it is acted upon in the manner indicated by the following equations:

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + HCl = \underset{\text{Monochlorhydrin.}}{C_3H_5Cl(OH)_2} + OH_2;$$

$$\underset{\text{Monochlorhydrin.}}{C_3H_5Cl(OH)_2} + HCl = \underset{\text{Dichlorhydrin.}}{C_3H_5Cl_2(OH)} + OH_2.$$

The term chlorhydrins or bromhydrins is applied to the bodies formed in this way from the polyhydric alcohols *in which one or more of the hydroxyl groups of the original alcohol still remain intact.* The term has, however, in one or two cases been improperly applied to the haloid derivative formed by the displacement of all the hydroxyl groups in an alcohol by chlorine or bromine, for example, the compound *trichloropropane,* $C_3H_5Cl_3$, derived from glycerin, is commonly known as trichlorhydrin. It is evident that the monohydric alcohols cannot yield chlorhydrins, since they only contain one OH group; they are consequently converted by the action of the haloid acids into mono-haloid derivatives of the corresponding hydrocarbons.

The chlorhydrins and bromhydrins are as a matter of fact simply the chlorinated and brominated derivatives of alcohols of lower hydricity than the parent alcohol. Thus the dichlorhydrin of glycerin, a trihydric alcohol, is the dichlorinated derivative of the monohydric propylic alcohol, as is shown by its conversion into that alcohol when acted upon by nascent hydrogen:

$$\underset{\text{Dichlorhydrin.}}{C_3H_5Cl_2.OH} + 2H_2 = \underset{\text{Propylic alcohol.}}{C_3H_7.OH} + 2HCl.$$

(1068) III. Ethers.—The ethers are a class of compounds which bear precisely the same relation to the alcohols that the metallic oxides bear to the metallic hydrates:—

	Alcohols.		Ethers.
$C_2H_5.OH$	Ethylic alcohol.	$(C_2H_5)_2O$	Ethylic oxide.
$C_2H_4(OH)_2$	Ethylenic alcohol.	C_2H_4O	Ethylenic oxide.
$C_3H_5(OH)_3$	Glyceric alcohol.	$(C_3H_5)_2O_3$	Glyceric oxide.
	Metallic hydrates.		Metallic oxides.
$NaOH$	Sodic hydrate.	Na_2O	Sodic oxide.
$Ca(OH)_2$	Calcic hydrate.	CaO	Calcic oxide.
$Bi(OH)_3$	Bismuthic hydrate.	Bi_2O_3	Bismuthic oxide.

It will be seen later on that not only are the methods by which it is possible to convert the alcohols into the corresponding ethers analogous to those which may be employed in the preparation of the metallic oxides from the metallic hydrates, but that they also bear considerable resemblance to the metallic oxides in chemical behaviour. For example, many of them are readily converted into the corresponding alcohols when heated with water just as under similar conditions, the metallic oxides are converted into hydrates:

$$\underset{\text{Ethylic oxide.}}{(C_2H_5)_2O} \quad + \quad OH_2 \quad = \quad \underset{\text{Ethylic alcohol.}}{2C_2H_5.OH.}$$

$$Na_2O \quad + \quad OH_2 \quad = \quad 2NaOH.$$

(1069) *Thioethers.*—These bear the same relation to the ethers that the thioalcohols do to the ordinary alcohols: they are the analogues of the metallic sulphides:

	Thioethers.		Metallic sulphides.
$(C_2H_5)_2S$	Ethylic sulphide	Na_2S	Sodic sulphide.
$(C_6H_5)_2S$	Phenylic sulphide		
C_2H_4S	Ethylenic sulphide	CaS	Calcic sulphide.

(1070) IV. Aldehydes.—The aldehydes are the characteristic oxidation products of the so-called primary alcohols, and are formed from the latter by the removal of hydrogen. This may be regarded as taking place in such a manner that the monad group, $CH_2.OH$, which is common to all the primary alcohols, is thereby converted into the group $(COH)'$; so that, if the primary alcohols be represented by such general formulæ as $R'(CH_2.OH)$, $R''(CH_2.OH)_2$, &c., the corresponding aldehydes will be represented by the formulæ $R'.COH$, $R''(COH)_2$, &c. The aldehydes may therefore be regarded as hydrocarbon derivatives formed by the displacement of hydrogen by the monad group, COH.

They are readily reconverted into the corresponding primary alcohol by the action of nascent hydrogen:

$$R'(COH) + H_2 = R'(CH_2.OH)$$

$$\underset{\text{Acetic aldehyde.}}{CH_3.COH} + H_2 = \underset{\text{Ethylic alcohol.}}{CH_3.CH_2OH}$$

With the exception of a few aldehydes of the form $R''(COH)_2$, all those at present known have been derived from, or correspond to, the primary monhydric alcohols which have the form $R'(CH_2.OH)$. The best known are the homologous aldehydes of the acetic and benzoic series, $C_nH_{2n+1}(COH)$ and $C_nH_{2n-7}(COH)$. Considerable interest attaches to this class of bodies from the numerous and interesting reactions in which they take part.

(1071) V. Acids.—Even at the present time the name "acid" is given in a very inconsequent manner to a large number of substances which have been shown to belong to totally distinct classes of compounds. In the case of the carbon compounds, however, chemists are beginning to appreciate the importance of precision in nomenclature, and to class as true acids only those compounds which behave similarly under certain test conditions.

Bodies are ordinarily said to be acids, or to have acid properties, if they are capable of yielding so-called metallic salts when acted upon by the metallic hydrates. There are many substances, however, such as phenol and alcohol, which possess this property, so that the capability of exchanging hydrogen for a metal is, if taken alone, an altogether insufficient criterion.

All the true acids, with which we are at present acquainted, may be included in one or other of the following groups:—

(1072) *a. Carboxylic or Carbo-Acids.*—When the aldehydes are carefully oxidized they unite with an amount of oxygen equivalent to the amount of hydrogen removed in their formation from the primary alcohols, and are converted into acids; for example:

$$\underset{\text{Ethylic alcohol.}}{C_2H_6O} - H_2 = \underset{\text{Aldehyde.}}{C_2H_4O}$$

$$\underset{\text{Aldehyde.}}{C_2H_4O} + O = \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

These acids are also formed by other methods besides that just described, and a consideration of these and of the behaviour of the bodies when submitted to the action of various reagents, have led chemists to the conclusion that just as the group $(CH_2.OH)'$ may be regarded as common to the primary alcohols, and the group $(COH)'$ as common to the aldehydes, so the group carboxyl $(CO.OH)'$ may be regarded as common to all acids which exhibit the behaviour of the acids derived from the primary alcohols by oxidation. The carboxylic acids may accordingly be represented by such general formulæ as $R'(CO.OH)'$, $R''(CO.OH)'_2$, $R'''(CO.OH)'_3$, &c. They form a most important group of carbon compounds, the greater number of the so-called organic acids at present known being carboxylic acids.

(1073) *b. Sulphonic or Sulpho-Acids.*—It is evident that the group $CO.OH$ may be viewed as formed from dibasic carbonic acid $CO(OH)_2$, by the removal of OH. The presence of the group $SO_2.OH$, which has the same relation to sulphuric acid, $SO_2(OH)_2$, as the group $CO.OH$ has to carbonic acid, $CO(OH)_2$, may be regarded as characteristic of the sulphonic acids or sulpho-acids, which are an important class of compounds. They are usually formed by the action of sulphuric acid on the hydrocarbons, &c., and are represented generally by such formulæ as $R'(SO_2.OH)$, $R''(SO_2.OH)_2$, &c.

(1074) *c. Sulphinic Acids.*—A few acids have been obtained of the form $R'(SO.OH)$, $R''(SO.OH)_2$, derived from sulphurous acid in the same way that the sulphonic acids are derived from sulphuric acid. They may be termed sulphinic acids. They are, however, of little interest, except from a theoretical point of view.

(1075) *d. Phosphonic Acids.*—The relation of these acids to phosphoric acid will be evident on inspection of the following formulæ:

$$\underset{\text{Phosphoric acid.}}{PO(OH)_3} \qquad ; \qquad \underbrace{R'.PO(OH)_2 \; ; \; R'_2.PO(OH)}_{\text{Phosphonic acids.}}$$

A very limited number of such acids have as yet been obtained.

As previously mentioned, there are various compounds which are frequently classed with the true acids, because they resemble them to a certain extent in their chemical behaviour, although their method of formation and the action of certain reagents on them show that they really belong to a different class of compounds.

The principal derivatives furnished by the carbo-acids are *metallic salts, haloid salts, ethereal salts, acid chlorides, bromides, and iodides, acid amides,* and *haloid derivatives.*

(1076) *Metallic Salts.*—One of the most characteristic properties which the acids possess is that of forming metallic salts when submitted to the action of metallic carbonates, the change consisting in the displacement of one or more hydrogen atoms in the acid by the equivalent amount of a metal. It is found that the maximum number of atoms of hydrogen thus displaceable, or, as it is termed, *the basicity of the acid*, is in direct relation to the number of COOH groups present in it; so that if an acid contains the carboxyl group, COOH, once it is said to be monobasic, if twice, dibasic, and so on. Those salts which are formed from the acids by the displacement of the maximum number of hydrogen atoms by metal are termed *normal salts*, whilst those salts which are formed by the displacement of a part only of the hydrogen are called *acid salts*. The composition of the normal salts of the monobasic, dibasic, and tribasic acids is represented by the general formulæ:

$$R'(CO.OM') \quad ; \quad R''(CO.OM')_2 \quad ; \quad R'''(CO.OM')_3,$$

where M is a monad metal; the composition of the acid salts of dibasic and tribasic acids containing monad metal being represented by the formulæ:

$$R''\left\{\begin{matrix}CO(OH)\\CO(OM')\end{matrix}\right. \quad ; \quad R'''\left\{\begin{matrix}CO(OH)\\CO(OH)\\CO(OM')\end{matrix}\right. \quad ; \quad R'''\left\{\begin{matrix}CO(OH)\\CO(OM')\\CO(OM')\end{matrix}\right. .$$

The normal salts of many of the monobasic acids also furnish so-called acid salts of the form $R'.CO(OM'), R'.CO(OH)$, such as the compound of acetic acid with potassic acetate, $CH_3.COOK, CH_3.COOH$; whilst the union of a normal salt with one or more molecules of metallic oxide produces a so-called basic salt, of which the basic plumbic acetates —$(C_2H_3O_2)_2Pb,PbO$ and $(C_2H_3O_2)_2Pb,2PbO$—may serve as examples.

(1077) *Haloid Salts.*—A haloid salt may be regarded as a normal metallic salt in which the metal is displaced by the equivalent quantity of a halogen. Comparatively few of these compounds are at present known. Schützenberger, however, has described the following, which are derivatives of acetic acid:

Chlorine acetate	$CH_3.CO(OCl)$.
Bromine ,, ...	$CH_3.CO(OBr)$.
Iodine ,, ...	$(CH_3.CO_2)_3I'''$.

The first two of these are the analogues of sodic acetate, $CH_3.CO(ONa)$, whilst the third is the analogue of bismuthic acetate, $(CH_3.CO_2)_3Bi'''$. These haloid salts, which are very unstable compounds, are never obtained by the action of the halogens on the acids.

(1078) *Ethereal Salts.*—These bodies, which are sometimes called compound ethers, are related to the alcohols in the same way that the metallic salts are to the metallic hydrates, and may consequently be regarded as formed from the acids by the displacement of H in the COOH group by the so-called positive alcohol radicles—thus:

$$\underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Sodic hydrate.}}{NaOH} = \underset{\text{Sodic acetate.}}{CH_3.COONa} + OH_2.$$

$$\underset{\text{Acetic acid.}}{CH_3.CO(OH)} + \underset{\text{Ethylic hydrate.}}{C_2H_5.OH} = \underset{\text{Ethylic acetate.}}{CH_3.CO(OC_2H_5)} + OH_2.$$

Normal and acid ethereal salts exist corresponding to the normal and acid metallic salts.

(1079) *Acid Chlorides, Bromides, and Iodides.*—These compounds are the characteristic products of the action of the haloid phosphorus compounds on the acids or their metallic salts. They are formed by the displacement of OH in the COOH group by chlorine, bromine, or iodine:

$$\underset{\text{Acetic acid.}}{3CH_3.CO(OH)} + PCl_3 = \underset{\text{Acetic chloride.}}{3CH_3.COCl} + PO_3H_3.$$

$$\underset{\text{Succinic acid.}}{C_2H_4(CO.OH)_2} + 2PCl_5 = \underset{\text{Succinic chloride.}}{C_2H_4(COCl)_2} + 2POCl_3 + 2HCl.$$

(1080) *Acid Amides.*—This name is applied to a class of compounds formed by the action of ammonia on the acid chlorides, or the normal ethereal salts, and also by distillation of the normal ammonic salts of the acids. We may consider them as formed from the acids by the displacement of OH in the COOH group by $(N'''H_2)'$:

$$\underset{\text{Acetic chloride.}}{CH_3.COCl} + 2NH_3 = \underset{\text{Acetamide.}}{CH_3.CO(NH_2)} + NH_4Cl.$$

$$\underset{\text{Ethylic acetate.}}{CH_3.CO(OC_2H_5)} + NH_3 = CH_3.CO(NH_2) + C_2H_5.OH.$$

$$\underset{\text{Ammonic acetate.}}{CH_3.CO(ONH_4)} = CH_3.CO(NH_2) + OH_2.$$

The so-called *amic acids* and *acid imides* are closely related to the acid amides. The nature of the relationship will be evident from the following formulæ:

Acid	$C_2H_4\left\{\begin{matrix}CO(OH)\\CO(OH)\end{matrix}\right.$	Succinic acid.
Amic acid . . .	$C_2H_4\left\{\begin{matrix}CO(NH_2)\\CO(OH).\end{matrix}\right.$	Succinamic acid.
Acid amide . . .	$C_2H_4\left\{\begin{matrix}CO(NH_2)\\CO(NH_2)\end{matrix}\right.$	Succinamide.
Acid imide . . .	$C_2H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH$	Succinimide.

(1081) *Haloid derivatives of the acids.*—By the action of chlorine or bromine on the acids one or more atoms of hydrogen may be displaced by the haloid, giving rise to comparatively stable haloid derivatives, *e.g.*:

$$\underset{\text{Acetic acid.}}{CH_3.COOH} + Cl_2 = \underset{\text{Monochloracetic acid.}}{CH_2Cl.COOH} + HCl.$$

$$\underset{\text{Monochloracetic acid.}}{CH_3Cl.COOH} + Cl_2 = \underset{\text{Dichloracetic acid.}}{CHCl_2.COOH} + HCl.$$

$$\underset{\text{Dichloracetic acid.}}{CHCl_2.COOH} + Cl_2 = \underset{\text{Trichloracetic acid.}}{CCl_3.COOH} + HCl.$$

Like the original acids these haloid derivatives are capable of yielding metallic and ethereal salts, acid chlorides, acid amides, &c.

Almost all the foregoing remarks on the carbo-acids apply generally to the sulphonic acids. As but few of the sulphinic and phosphonic acids are at present known, it will be better to consider their characteristic properties when the individual compounds are described.

(1082) VI. ACID ANHYDRIDES.—These compounds, which may generally be obtained by the action of the acid chlorides on the acids, bear the same relation to the acids that the ethers do to the alcohols:—

$$\underset{\text{Acetic acid.}}{CH_3.CO(OH)}\ ;\ \underset{\text{Acetic anhydride.}}{\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O}\ .\ \underset{\text{Alcohol.}}{C_2H_5.OH}\ ;\ \underset{\text{Ether.}}{\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.}$$

$$\underset{\text{Succinic acid.}}{C_2H_4\left\{\begin{matrix}CO(OH)\\CO(OH)\end{matrix}\right.}\ ;\ \underset{\text{Succinic anhydride.}}{C_2H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}O}\ .\ \underset{\text{Ethylenic alcohol.}}{C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.}\ ;\ \underset{\text{Ethylenic oxide or ether.}}{C_2H_4O.}$$

They are reconverted into acids by the action of water.

(1083) VII. KETONES.—The ketones or acetones are a class of compounds closely related to the aldehydes, and may be regarded as derived from them by the displacement of H in the

COH group by the so-called positive alcohol radicles; thus we have

$CH_3.CO(CH_3)$ Dimethylketone.	derived from	$CH_3.COH$ Aldehyde.
$C_6H_5.CO(CH_3)$ Methylphenyl ketone.	„	$C_6H_5.COH$ Benzoic aldehyde.

Although the ketones closely resemble the aldehydes in many respects, they may be distinguished from them by their behaviour with oxidizing agents; the aldehydes yielding an acid containing the same number of carbon atoms as the original compound, whilst the ketones are converted into acids containing fewer atoms of carbon in the molecule than the original ketone.

(1084) VIII. Amines and Allied Compounds.—The compounds included in this most important class are generally regarded as derivatives of ammonia in which a part or the whole of the hydrogen is displaced by hydrocarbon groups, or so-called positive alcohol radicles. They are known as *monamines, diamines,* or *triamines,* according as they are derived from a single molecule, two molecules, or three molecules of ammonia. Moreover, primary, secondary, and tertiary monamines, diamines, and triamines are distinguished; the primary amines being formed by the displacement of one-third, the secondary amines by the displacement of two-thirds, and the tertiary amines by the displacement of the whole of the hydrogen in the one, two, or three molecules of ammonia, as the case may be. A few compounds intermediate in composition between the primary and secondary and secondary and tertiary amines are also known. The composition of the more general forms of amines is given by the following general formulæ, in which the symbols R′, R″, R‴, indicate respectively a monad dyad, and triad radicle:—

	Primary.	Secondary.	Tertiary.
Monamines.	$N\left\{\begin{matrix}R'\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}R'\\R'\\H\end{matrix}\right.$	$N\left\{\begin{matrix}R'\\R'\\R'\end{matrix}\right.$ $N\left\{\begin{matrix}R''\\R'\end{matrix}\right.$ NR'''
Diamines.	$N_2\left\{\begin{matrix}R''\\H_2\\H_2\end{matrix}\right.$	$N_2\left\{\begin{matrix}R''\\R''\\H_2\end{matrix}\right.$ $N_2\left\{\begin{matrix}R''\\R'_2\\H_2\end{matrix}\right.$	$N_2\left\{\begin{matrix}R'''\\R'_2\\H\end{matrix}\right.$ $N_2\left\{\begin{matrix}R''\\R''\\R''\end{matrix}\right.$ $N_2\left\{\begin{matrix}R''\\R'_2\\R_2\end{matrix}\right.$
Triamines.	$N\left\{\begin{matrix}R'''\\H_3\\H_3\end{matrix}\right.$ $N_3\left\{\begin{matrix}R^{IV}\\H_2\\H_3\end{matrix}\right.$	$N_3\left\{\begin{matrix}R^{IV}\\R'_2\\H_3\end{matrix}\right.$	$N_3\left\{\begin{matrix}R'''\\R'''\\R'''\end{matrix}\right.$

The primary amines may also be regarded as amidogen (NH_2) derivatives of the hydrocarbons—that is to say, as formed from the hydrocarbons by the displacement of one or more atoms of hydrogen by the same number of monad NH_2 groups. For example, aniline may be represented either as derived from ammonia, NH_3, by the displacement of one of the hydrogen atoms by the radicle phenyl, C_6H_5, thus: $N\left\{\begin{matrix}H\\H\\C_6H_5\end{matrix}\right.$ (*phenylamine*), or as derived from benzene, C_6H_6, by the displacement of the hydrogen atom by the monad amidogen group NH_2, thus: $C_6H_5(NH_2)'$ (*amidobenzene*).

The amines, as a rule, combine directly with the acids to form substituted ammonium salts, from which the amine can again be liberated on the addition of an alkali. Thus:

$$\underset{\text{Ethylamine.}}{C_2H_5NH_2} + HCl = \underset{\text{Ethylammonic chloride.}}{C_2H_5.NH_3Cl.}$$

$$\underset{\text{Ethylammonic chloride.}}{C_2H_5.NH_3Cl} + KOH = \underset{\text{Ethylamine.}}{C_2H_5.NH_2} + KCl + OH_2.$$

Or generally

$$R'.N'''H_2 + HCl = R'.N^{v}H_3Cl.$$

$$R'.N^{v}H_3Cl + KOH = R'.N'''H_2 + KCl + OH_2.$$

The diamines and triamines can combine respectively with at most two and three molecules of a monobasic acid: many, however, do not unite with so large a proportion of acid.

Many of the tertiary amines combine directly with the haloid hydrocarbon derivatives, such as ethylic iodide, C_2H_5I, and ethylenic bromide, $C_2H_4Br_2$, thus:

$$\underset{\text{Triethylamine.}}{N(C_2H_5)_3} + C_2H_5I = \underset{\text{Tetrethylammonic iodide.}}{N(C_2H_5)_4I.}$$

When the compounds so produced are treated with moist argentic oxide the halogen is replaced by OH, and bodies are obtained which may be regarded as derivatives of ammonic hydrate, $NH_4.OH$:

$$\underset{\text{Tetrethylammonic iodide.}}{2N(C_2H_5)_4I} + Ag_2O + OH_2 = \underset{\text{Tetrethylammonic hydrate.}}{2N(C_2H_5)_4.OH} + 2AgI.$$

These compounds closely resemble ammonic hydrate and the alkaline hydrates in chemical behaviour, precipitating the various metals from their solutions as hydrates, &c.

Bodies corresponding to the amines have been obtained containing phosphorus, arsenic, or antimony in place of the nitrogen.

(1085) IX. Organo-Metallic Compounds.—These are conveniently regarded as compounds of the metals with monad hydrocarbon groups, the so-called positive alcohol radicles. The following is a list of some of the principal members of this class of compounds:

$Zn(CH_3)_2$	Zinc methyl	or	Zincic methide.
$Zn(C_2H_5)_2$	„ ethyl	„	„ ethide.
$Hg(C_2H_5)_2$	Mercury ethyl	„	Mercuric ethide.
$Hg(C_6H_5)_2$	„ phenyl	„	„ phenide
$Hg(C_{10}H_7)_2$	„ naphthyl	„	„ naphthide
$Bi(C_2H_5)_3$	Bismuth ethyl	„	Bismuthic ethide
$Pb(C_2H_5)_4$	Lead ethyl	„	Plumbic ethide.
$Sn(C_2H_5)_2$		„	Stannous ethide.
$Sn(C_2H_5)_4$		„	Stannic ethide.
$Sn_2(C_2H_5)_6$		„	Distannic hexethide.

In addition to the substances which may with certainty be referred to one or other of the above well-defined classes, there are many compounds which exhibit the distinctive characters of more than one class: *lactic acid,* $C_2H_4(OH).COOH$, for example, may be said to be both acid and alcohol, exhibiting, as it does, the properties of both classes of compounds. Again, the compound $C_6H_4(NH_2).COOH$, *amidobenzoic acid,* is at the same time amine and acid; for like all bodies which contain the CO.OH group, it is capable of yielding a series of metallic salts, and like the amines it is also capable of combining with acids. It will be unnecessary to form special classes to include such compounds, as they may be most conveniently arranged as subsidiary groups derived from the members of the primary series. Thus the acids like lactic acid are most conveniently treated as monoxy-derivatives of the acids of the acetic series, and bodies such as amidobenzoic acid as amido-derivatives of the acids of the benzoic series.

The simple nature of the relation between the corresponding terms of the heterologous* series above defined will be better appreciated on inspection of the table given on pp. 64, 65, in which the different classes of compounds are so arranged that all those bodies which are placed in the same vertical column are homologous, or similar in constitution; whilst those which are placed in different columns are heterologous or dissimilar in constitution and in chemical characters.

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* From ἕτερος different, and λόγος—a term applied to bodies which, although nearly related to one another, have a different constitution.

Table to Illustrate the Arrangement of

Hydrocarbons.	Monohaloid-derivatives.	Amines.	Alcohols.	Thioalcohols.	Ethers.
C_nH_{2n+2}.	$C_nH_{2n+1}Cl$.	$C_nH_{2n+1}.NH_2$.	$C_nH_{2n+1}.OH$.	$C_nH_{2n+1}.SH$.	$(C_nH_{2n+1})_2O$.
1. CH_4	CH_3Cl	$CH_3.NH_2$	$CH_3.OH$	$CH_3.SH$	$(CH_3)_2O$
2. C_2H_6	C_2H_5Cl	$C_2H_5.NH_2$	$C_2H_5.OH$	$C_2H_5.SH$	$(C_2H_5)_2O$
3. C_3H_8	C_3H_7Cl	$C_3H_7.NH_2$	$C_3H_7.OH$	$C_3H_7.SH$	$(C_3H_7)_2O$
4. C_4H_{10}	C_4H_9Cl	$C_4H_9.NH_2$	$C_4H_9.OH$	$C_4H_9.SH$	$(C_4H_9)_2O$
5. C_5H_{12}	$C_5H_{11}Cl$	$C_5H_{11}.NH_2$	$C_5H_{11}.OH$	$C_5H_{11}.SH$	$(C_5H_{11})_2O$
6. C_6H_{14}	$C_6H_{13}Cl$	$C_6H_{13}.NH_2$	$C_6H_{13}.OH$	$C_6H_{13}.SH$	
7. C_7H_{16}	$C_7H_{15}Cl$		$C_7H_{15}.OH$		
8. C_8H_{18}	$C_8H_{17}Cl$		$C_8H_{17}.OH$		
9. C_9H_{20}	$C_9H_{19}Cl$		$C_9H_{19}.OH$		
10. $C_{10}H_{22}$	$C_{10}H_{21}Cl$		$C_{10}H_{21}.OH$		

§ III. THEORY OF COMPOUND RADICLES.

(1086) Liebig explained the similarity in properties between the terms of homologous series by supposing the existence in each, of a certain group of elements which he regarded as the radicle of the series. In fact, he made the theory of *compound radicles*,* as it is termed, the basis of his classification, and defined organic chemistry to be the chemistry of compound radicles. According to this supposition, the basis of each ether, for example, is a hydrocarbon, from which all the *heterologous* bodies of the series, or bodies not analogous in composition are derived; thus:

Compound Radicle.		*Ether or Oxide of the Radicle.*	
Methyl	CH_3	Methylic ether .	$(CH_3)_2O$
Ethyl	C_2H_5	Ethylic ether .	$(C_2H_5)_2O$
Amyl	C_5H_{11}	Amylic ether .	$(C_5H_{11})_2O$

Alcohol, or Hydrated Oxide.

Methylic alcohol (wood spirit) . . .	$CH_3.OH$
Ethylic alcohol (alcohol)	$C_2H_5.OH$
Amylic alcohol (fusel oil)	$C_5H_{11}.OH$

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* The German term *radikal* (from the Latin *radix*, a root) is commonly, but inaccurately, translated *radical*, which is properly an adjective, the word *radicle* being the appropriate rendering. A radicle may consist of a single elementary atom, and it then forms a simple radicle; or it may consist of a group of atoms, in which case it constitutes a compound radicle.

According to this theory each simple ether is the oxide of the electro-positive hydrocarbon which forms the radicle of the series; the corresponding alcohol is the hydrated oxide of the same radicle, and the mono-haloid derivatives or so-called hydrochloric, hydrobromic, and hydriodic ethers, are compounds in which chlorine, bromine, or iodine have united with the radicle—just as in the corresponding compounds of a metal; in the ethyl series, for instance, the compound group termed ethyl, C_2H_5, discharges a function in these compounds analogous to that of potassium in the salts of this metal, so that representing ethyl, C_2H_5, by Et, the two series would run as follows:

Heterologous Compounds in Homologous Series.

Thioethers. $(C_nH_{2n+1})_2S$.	Aldehydes. $C_nH_{2n+1}.COH$.	Ketones. $(C_nH_{2n+1})_2CO$	Acids. $C_nH_{2n+1}CO(OH)$	Anhydrides. $(C_nH_{2n+1}CO)_2O$	Organo-metallic compounds. $(C_nH_{2n+1})_2Zn$.
$(CH_3)_2S$	$CH_3.COH$	$(CH_3)_2CO$	$CH_3.CO(OH)$	$(CH_3.CO)_2O$	$(CH_3)_2Zn$
$(C_2H_5)_2S$	$C_2H_5.COH$	$(C_2H_5)_2CO$	$C_2H_5.CO(OH)$	$(C_2H_5.CO)_2O$	$(C_2H_5)_2Zn$
$(C_3H_7)_2S$	$C_3H_7.COH$	$(C_3H_7)_2CO$	$C_3H_7.CO(OH)$	$(C_3H_7.CO)_2O$	$(C_3H_7)_2Zn$
$(C_4H_9)_2S$	$C_4H_9.COH$	$(C_4H_9)_2CO$	$C_4H_9.CO(OH)$	$(C_4H_9.CO)_2O$	$(C_4H_9)_2Zn$
$(C_5H_{11})_2S$	$C_5H_{11}.COH$	$(C_5H_{11})_2CO$	$C_5H_{11}.CO(OH)$	$(C_5H_{11}.CO)_2O$	$(C_5H_{11})_2Zn$
	$C_6H_{13}.COH$		$C_6H_{13}.CO(OH)$		
	$C_7H_{15}.COH$		$C_7H_{15}.CO(OH)$		
	$C_8H_{17}.COH$		$C_8H_{17}.CO(OH)$		
	$C_9H_{19}.COH$	$(C_9H_{19})_2CO$	$C_9H_{19}.CO(OH)$		
			$C_{10}H_{21}.CO(OH)$		

Potassic chloride .	KCl	Ethylic chloride .	EtCl
Potassic iodide .	KI	Ethylic iodide . .	EtI
Potassic hydrate .	KOH	Ethylic hydrate .	EtOH
Potassic oxide . .	K_2O	Ethylic oxide . .	Et_2O

It is true that the theory of compound radicles supposes the existence of a number of substances which have not been isolated, and which have no separate existence. Gerhardt, however, who is usually followed by later writers, expressly rejects isolability as constituting any part of his idea of a radicle (*Traité*, t. iv. p. 569). He says: "Let it be clearly understood that, in speaking of a radicle, I do not indicate any substance under the form and with the properties which it would have in an isolated condition; but I distinguish by it simply the proportion in which certain elements, or groups of elements, may be substituted for others, or may be transferred from one body to another in the process of double decomposition." The theory, indeed, cannot be supposed to afford a correct representation of the constitution of organic bodies; but it is a convenient fiction, which materially facilitates the retention of their composition in the memory, and the comprehension of the changes which such compounds undergo. One of the first groups to which it was systematically applied by Liebig and Wöhler was that derived from the essential oil of bitter almonds. This oil was regarded by these chemists as containing an organic radicle, to which they gave the name of *benzoyl*, C_7H_5O, and which may be conveniently distinguished by the symbol Bz. Although unsuccessful in the attempt to isolate this radicle, they succeeded in transferring the group of which it was supposed to consist from one elementary substance to another, and in causing it to enter into combination with other groups; and by the aid of this hypothesis they were enabled to give as simple and intelligible an account of the mode in which the compounds derived from the oil were formed, as though they had been dealing with the salts or other compounds of a metal. The advantages thus obtained may be rendered evident by comparing the empirical formulæ of some of these compounds with those in which the same bodies are represented as containing the organic radicle:

	Empirical Formula.	$C_7H_5O = Bz$	
Oil of bitter almonds .	C_7H_6O	BzH .	Benzoyl hydride
Benzoic acid	$C_7H_6O_2$	BzOH .	Benzoyl hydrate
Chlorinated compound .	C_7H_5OCl	BzCl .	Benzoyl chloride
Sulphur compound . .	$C_{14}H_{10}O_2S$	Bz_2S .	Benzoyl sulphide
Cyanogen compound .	C_8H_5ON	BzCN .	Benzoyl cyanide

It is, moreover, to be observed, that many substances corresponding in composition to certain of the organic radicles may be isolated. The existence of cyanogen as an electro-negative organic radicle, and the remarkable analogy in its mode of combination to that of chlorine and the halogens, were known long before Liebig had attempted to generalize the theory of organic radicles.

A large number of the hydrocarbon radicles which have at present been studied are monads, others are dyads, and a few are triads. No isolated radicle is known, the molecule of which contains an *uneven* number of atoms of hydrogen; though so-called isolated radicles with an even number of atoms of hydrogen are of frequent occurrence.

1. All radicles hitherto admitted of the form C_nH_{2n+1}, such as methyl, CH_3, ethyl, C_2H_5, or amyl, C_5H_{11}, are *monads:* as is seen in ethylic chloride, C_2H_5Cl, and amylic iodide, $C_5H_{11}I$; and in isolated ethyl or ethylic ethide, $C_2H_5.C_2H_5$.

2. Radicles of the form C_nH_{2n}, such as ethylene, C_2H_4, propylene, C_3H_6, and octylene, C_8H_{16}, are *dyad*, as in ethylenic chloride, $C_2H_4Cl_2$. Such radicles may exist in the free state.

3. A radicle of the form C_nH_{2n-1} is in certain cases *triad*, in others *monad;* C_3H_5, for example, is triad in glycerin, $C_3H_5(OH)_3$, but monad in allylic alcohol, $C_3H_5.OH$, and in allylic chloride, C_3H_5Cl.

A radicle may as a rule be made to change its valency, or, as it is sometimes called, its basicity, by the removal of hydrogen, the valency being increased by unity for each atom of hydrogen which is withdrawn. As an example of this we may take methane or marsh gas, which is a saturated body:* by acting upon this gas with chlorine, 1, 2, 3, and 4 atoms of hydrogen may be removed in succession, and a corresponding number of atoms of chlorine substituted:

Methane (methylic hydride)	CH_4
Monochloromethane (methylic chloride)	CH_3Cl
Dichloromethane (methylenic chloride)	CH_2Cl_2
Trichloromethane (chloroform)	$CHCl_3$
Tetrachloromethane (carbonic tetrachloride)	CCl_4

These four derivatives of methane may be regarded respectively as compounds of the following four radicles with chlorine:

Monad	$(CH_3)'$	or	C_nH_{2n+1}
Dyad	$(CH_2)''$	or	C_nH_{2n}
Triad	$(CH)'''$	or	C_nH_{2n-1}
Tetrad	C^{iv}		

(1087) *Chemical Types.*—The various homologous series of bodies in the table on pp. 64, 65 have their representatives among the simpler so-called inorganic compounds; thus, for example, by deducting CH_2 from the formula of methane and the compounds derived from it contained in the horizontal line 1 in the table, we arrive at hydrogen and some of its most important compounds of simple constitution:—The molecule of methane if deprived of CH_2, would leave a residue consisting of hydrogen only: $CH_4 - CH_2 = H_2$; the molecule of monochloromethane deprived of CH_2 would leave hydrochloric acid: $CH_3Cl - CH_2 = HCl$; the molecule of methylic alcohol and of methylic oxide or ether deprived of CH_2 would leave water: $CH_3.OH - CH_2 = OH_2$; and, similarly, the residue from each molecule of methylic sulphydrate, $CH_3.SH$, and of methylic sulphide, $(CH_3)_2S$, would be hydric sulphide, SH_2.

Hence it appears that the hypothetical radicles methyl, ethyl, propyl, tetryl or butyl, pentyl or amyl, &c., are bodies which correspond to hydrogen, and that they may be regarded as homologues of a series in which hydrogen forms the lowest term: that the monochlorinated hydrocarbons are the homologues of hydrochloric acid, whilst the alcohols and ethers are homologues of water, and the mercaptans and sulphides homologues of hydric sulphide. Hydrochloric acid, water, and hydric sulphide may, therefore, be regarded as the patterns or *types* upon which these several bodies are formed.

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* By a saturated molecule is here understood a compound which will not unite directly with an elementary monad, or a monad radicle: whenever it forms compounds, such compounds are produced by substitution, methylic chloride CH_3Cl, for example, being obtained from methane by substituting 1 atom of chlorine for 1 of hydrogen.

This idea of referring organic compounds to some simple representative or type was systematically worked out by Laurent and by Gerhardt.

The four principal types to which most of the compounds of organic chemistry may be referred are the following:

1. The hydrogen or metallic type . $\left.\begin{matrix}H'\\H'\end{matrix}\right\}$, or H_2;
2. The oxide or water type. . . $\left.\begin{matrix}H'\\H'\end{matrix}\right\}O''$, or H_2O;
3. The nitride or ammonia type . $\left.\begin{matrix}H'\\H'\\H'\end{matrix}\right\}N'''$, or H_3N;
4. The marsh gas type . . . . $\left.\begin{matrix}H'\\H'\\H'\\H'\end{matrix}\right\}C^{iv}$, or H_4C.

It is important to remark, that many bodies are referred to the same type, though they present no analogy in chemical properties, either to it or to each other, and though the various radicles which are assumed to exist in organic compounds vary in character as much as the elementary bodies themselves.

When we compare different compounds belonging to the same series, a progressive change in properties is observed, so that the differences between any two such compounds become greater, the wider is the interval between the respective places in the series of the two terms submitted to comparison. Following this idea to its extreme limits, the same type may therefore comprehend bodies belonging to the three classes of acids, of bases, and of neutral bodies; the acids or electro-negative bodies being at one extremity of the series, and the bases or electro-positive bodies at the opposite extremity, the neutral bodies occupying the intermediate positions.

The application of these types to carbon compounds will be best understood by means of a few examples:

1. *The Hydrogen or Metallic type*, $\left\{\begin{matrix}H'\\H'.\end{matrix}\right.$

To this class may be referred the monad metals, as well as the dyad metals, such as zinc and cadmium, of which the molecule is monatomic; and amongst organic compounds, the hypothetical radicles of the monohydric alcohols, certain bodies formed by the union of two different monad radicles, such as the aldehydes and the ketones, as well as the dyad organic radicles such as ethylene:

Potassium	$\left\{\begin{matrix}K\\K\end{matrix}\right.$
Zinc	Zn''
Dimethyl (ethane)	$\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$
Aldehyde (acetic hydride).	$\left\{\begin{matrix}C_2H_3O\\H\end{matrix}\right.$

Acetone (acetic methide) . . . . $\left\{\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right.$

Ethylene (olefiant gas) . . . . C_2H_4

Hydrochloric acid was originally proposed by Gerhardt as an additional typical body, but the *hydrochloric acid type*, $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, is now usually included under the hydrogen type. It forms a subtype which comprehends the monohaloid derivatives of the hydrocarbons, including, therefore, the so-called haloid ethers, and the chlorides of the hypothetical radicles of the monobasic acids; for example:

Ethylic chloride (monochlorethane) . . . . $\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right.$

Benzoic chloride (benzoyl chloride) . . . . $\left\{\begin{matrix}C_7H_5O\\Cl\end{matrix}\right.$

Acetic chloride (acetyl chloride) . . . . . $\left\{\begin{matrix}C_2H_3O\\Cl\end{matrix}\right.$

2. *The Water type* . . . . $O''\left\{\begin{matrix}H'\\H'.\end{matrix}\right.$

This type includes the oxides, sulphides, selenides, and tellurides of all the monad radicles, such as the alcohols and mercaptans, the ethers and thioethers, the so-called compound ethers, and the monobasic organic acids and their anhydrides; for instance:

Methylic alcohol (wood spirit) . . . . . $O\left\{\begin{matrix}CH_3\\H\end{matrix}\right.$

Ethylic alcohol (alcohol) . . . . $O\left\{\begin{matrix}C_2H_5\\H\end{matrix}\right.$

Ethylic sulphydrate (mercaptan) . . . . $S\left\{\begin{matrix}C_2H_5\\H\end{matrix}\right.$

Ethylic oxide (ordinary ether) . . . . . . $O\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$

Ethylic sulphide . . . . $S\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$

Acetic acid . . . . $O\left\{\begin{matrix}C_2H_3O\\H\end{matrix}\right.$

Ethylic acetate (acetic ether) . . . . . . $O\left\{\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right.$

Acetic acetate (acetic anhydride) . . . . $O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right.$

Tetrethylammonic hydrate. . . . . $O\left\{\begin{matrix}(CH_3)_4N\\H\end{matrix}\right.$

3. *The Ammonia type* $\left.\begin{matrix}H'\\H'\\H'\end{matrix}\right\}N'''$ includes the nitrides and phosphides, as well as arsenides and antimonides, of the alcohol radicles, together with the amines, and the amides:

Ethylamine. . . . . $N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$

Diethylphosphine . . . . $P\left\{\begin{array}{l} C_2H_5 \\ C_2H_5 \\ H \end{array}\right.$

Trimethylamine . . . . $N\left\{\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right.$

Acetamide . . . . $N\left\{\begin{array}{c} C_2H_3O \\ H \\ H \end{array}\right.$

4. *The Marsh Gas type* . . . . $C^{iv}\left\{\begin{array}{l} H \\ H \\ H \\ H \end{array}\right.$

comprises compounds like carbonic anhydride, ethylic orthocarbonate, silicic chloride, and plumbic tetrethide:

$$C^{iv}\left\{\begin{array}{l} O'' \\ O'' \end{array}\right. \qquad C^{iv}\left\{\begin{array}{l} (OC_2H_5)' \\ (OC_2H_5)' \\ (OC_2H_5)' \\ (OC_2H_5)' \end{array}\right. \qquad Si^{iv}\left\{\begin{array}{l} Cl \\ Cl \\ Cl \\ Cl \end{array}\right.$$

Carbonic anhydride. Ethylic orthocarbonate. Silic chloride.

$$Pb^{iv}\left\{\begin{array}{l} (C_2H_5)' \\ (C_2H_5)' \\ (C_2H_5)' \\ (C_2H_5)' \end{array}\right.$$

Plumbic tetrethide.

A large number of bodies may be regarded as formed upon condensed types, or upon the plan of the preceding types, doubled, tripled, quadrupled, &c. For instance, sulphuric acid and glycol may be regarded as formed from two molecules of water, the dyad group SO_2 in the one case, and C_2H_4 in the other, forming the link which by displacing one atom of hydrogen in each molecule of water, connects or binds the two residues or radicles OH together; thus:

$$\begin{array}{l} O\left\{\begin{array}{l} H \\ H \end{array}\right. \\ O\left\{\begin{array}{l} H \\ H \end{array}\right. \end{array} \qquad \begin{array}{ll} O\,\{ & H \\ & SO_2 \\ O\,\{ & H \end{array} \qquad \begin{array}{ll} O\,\{ & H \\ & C_2H_4 \\ O\,\{ & H \end{array}$$

2 Molecules of Water. Sulphuric Acid. Glycol.

In like manner, urea may be supposed to be formed in the same way upon the type of two molecules of ammonia:

$$\begin{array}{l} N\left\{\begin{array}{l} H \\ H \\ H \end{array}\right. \\ N\left\{\begin{array}{l} H \\ H \\ H \end{array}\right. \end{array} \qquad \begin{array}{ll} N\left\{\begin{array}{l} H \\ H \end{array}\right. & \\ & CO \\ N\left\{\begin{array}{l} H \\ H \end{array}\right. & \end{array}$$

2 Molecules of Ammonia. Urea.

These condensed types can only be employed in the case of compounds which contain multivalent radicles, such as sulphuryl, SO_2, ethylene, C_2H_4, and carbonyl, CO, as in the instance just cited, where the radicle serves as the link to bind the several radicles into one.

It will be seen that each of the four substances, hydrogen, water, ammonia, and marsh gas, thus selected as types to one of which the various chemical compounds are referred, is a compound of hydrogen ; and that other bodies are supposed to be formed from these typical substances by the substitution of a portion, or of the whole, of the hydrogen of the type by simple or compound radicles. For the sake of precision it is often found to be necessary to distinguish the unaltered hydrogen of the type from any hydrogen which may have been subsequently introduced into the molecule. Alcohol, for example, is said to be a compound formed upon the water type by the introduction of the radicle ethyl, C_2H_5, in the place of one of the original atoms of hydrogen in the type: alcohol being $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, whilst water is $\left.\begin{matrix}H\\H\end{matrix}\right\}O$. In such cases the original hydrogen in the type is distinguished as *typical* hydrogen.

Many compounds not included under the preceding types, may be referred to the union of two of the foregoing types, as was first suggested by Williamson, such compounds being represented as derived from *mixed types*. Kekulé, for example (*Lehrbuch der Org. Chemie*, i. p. 121,) proposed to consider the amic acids, such as carbamic and oxamic acid, as formed upon the combination of the types of ammonia and water:

$$\begin{array}{l}N\left\{\begin{array}{l}H\\H\\H\end{array}\right.\\O\left\{\begin{array}{l}H\\H\end{array}\right.\end{array}\qquad\begin{array}{l}N\left\{\begin{array}{l}H\\H\end{array}\right.\\ \quad(CO)''\\O\left\{\begin{array}{l}H\end{array}\right.\end{array}\qquad\begin{array}{l}N\left\{\begin{array}{l}H\\H\end{array}\right.\\ \quad(C_2O_2)'';\\O\left\{\begin{array}{l}H\end{array}\right.\end{array}$$

Double type. Carbamic acid. Oxamic acid.

the tie between the two typical groups being in the one case the dyad radicle CO, in the other C_2O_2.

CHAPTER III.

ACTION OF REAGENTS ON CARBON COMPOUNDS.

IN investigating the chemical nature of the carbon compounds, and the relation they bear to one another and to the so-called inorganic compounds, it is usual to treat them with a variety of reagents; many of these attack the individual members of various classes of organic compounds much in the same way, so that it will be convenient in this place to describe the general action of the most important of them.

(1088) *Oxidizing Agents.*—It will be unnecessary to consider minutely the effects of rapid direct oxidation, or combustion, since the general result in all cases where there is a sufficient supply of oxygen is to convert the carbon into carbonic anhydride, and the hydrogen into water; the nitrogen is generally liberated in the free state.

It is not merely to the processes of oxidation effected in the laboratory that it is necessary to attend, for oxidizing actions are in constant operation unperceived on every side of us. The gradual decay of organized compounds is caused by the spontaneous oxidation which slowly takes place: decay being in reality, only a slow process of combustion, a fact which Liebig indicated by substituting the term *eremacausis* for that of decay (from ἤρεμος, gentle, καῦσις, combustion). The decay of wood is a familiar instance of this kind; the hydrogen of the wood becomes more rapidly oxidized than its carbon, and the result is the formation of a brown powder termed ulmin or humus, in which the proportion of the carbon to the hydrogen and the oxygen is much greater than in the wood from which it was formed. Such actions take place generally under the combined influence of moisture and of a temperature of about 15° (59° F.) or upwards. If the substance be perfectly dry, or if the temperature fall to the freezing point, oxidation is usually completely arrested.

It is, however, the study of the process of gradual or limited oxidation which affords results so instructive to the chemist: this is seldom effected by the action of free oxygen, but by the use of certain reagents which present that element in the nascent state. The most ordinary sources of oxygen employed for this purpose are nitric acid, a mixture of sulphuric acid and potassic dichromate, a mixture of sulphuric acid and manganic peroxide, chromic anhydride, dissolved either in water or in glacial acetic acid, potassic permanganate, argentic oxide, and plumbic peroxide. Besides these, other oxidizing agents are occasionally used, such as ferric chloride, baric peroxide, calcic hypochlorite, and fused potassic and sodic hydrates; the last three of these are of more limited application, however, since they frequently give rise to secondary reactions. Sulphuric acid, at a high temperature, also readily parts with a portion of its oxygen, but in this case the results are usually complicated by the powerful dehydrating action of the acid.

The effect produced by these different means of oxidation varies considerably with the nature of the compound submitted to their action, and also with that of the oxidizing agent.

1. The oxygen may simply remove hydrogen; as when alcohol is submitted to the oxidizing action of chromic acid. In

this case water is formed, and a new body, aldehyde, is produced, containing less hydrogen than alcohol:

$$\underset{\text{Ethylic alcohol.}}{2C_2H_6O} + O_2 = \underset{\text{Aldehyde.}}{2C_2H_4O} + 2OH_2.$$

2. Oxygen may unite directly with the substance; as when aldehyde is converted into acetic acid:

$$\underset{\text{Aldehyde.}}{2C_2H_4O} + O_2 = \underset{\text{Acetic acid.}}{2C_2H_4O_2}.$$

3. Hydrogen is eliminated and replaced by an equivalent quantity of oxygen; for example, when benzylbenzene is oxidized by chromic acid solution, it yields phenylbenzoyl:

$$\underset{\text{Benzylbenzene.}}{C_{13}H_{12}} + O_2 = \underset{\text{Phenylbenzoyl.}}{C_{13}H_{10}O} + OH_2.$$

4. Hydrogen is eliminated and replaced by twice its equivalent quantity of oxygen; as in the formation of the quinones by the direct oxidation of the corresponding hydrocarbons. Thus, naphthalene when treated with a solution of chromic anhydride in glacial acetic acid gives naphthaquinone:

$$\underset{\text{Naphthalene.}}{2C_{10}H_8} + 3O_2 = \underset{\text{Naphthaquinone.}}{2C_{10}H_6O_2} + 2OH_2;$$

and toluene when treated with dilute nitric acid gives benzoic acid:

$$\underset{\text{Toluene.}}{2C_7H_8} + 3O_2 = \underset{\text{Benzoic acid.}}{2C_7H_6O_2} + 2OH_2.$$

$$2C_6H_5.CH_3 + 3O_2 = 2C_6H_5.COOH + 2OH_2.$$

In this case, however, it is probable that two of the atoms of hydrogen in the methyl group, CH_3, of the toluene are eliminated and displaced by an atom of oxygen, whilst the remaining atom of hydrogen is displaced by the group OH.

In all the cases we have hitherto considered the carbon in the original substance is unaffected by the process of oxidation, the number of atoms of that element in the oxidized product being the same as in the compound we started with. There are many instances, however, in which the substance splits up under the influence of the oxidizing action, giving rise to two or more compounds, each containing a smaller number of carbon atoms than the original substance. Thus, acetone yields acetic acid and carbonic anhydride:

$$\underset{\text{Acetone.}}{C_3H_6O} + 2O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + CO_2 + OH_2.$$

Similarly, the tertiary butylic alcohol, trimethylcarbinol, is converted into formic and acetic acids :

$$\underset{\text{Trimethylcarbinol.}}{C_4H_{10}O} + 3O_2 = \underset{\text{Formic acid.}}{2CH_2O_2} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + OH_2.$$

Contact with a body which is itself undergoing slow oxidation will frequently induce this oxidizing action in substances possessed of a strong attraction for oxygen, but which do not, when in a pure state, themselves undergo oxidation. For example, a solution of grape sugar in an alcoholic solution of potassic hydrate does not absorb oxygen when exposed to the air; but the addition of a minute quantity of sulphindylic acid (indigosulphonic acid: see indigo) effects the oxidation of the sugar: probably, as Traube suggests, by the absorption of oxygen on the part of the sulphindylic acid, and the transfer of oxygen to the sugar; the sulphindylic acid absorbing fresh oxygen and again parting with it to fresh portions of sugar, acting, in fact, as a carrier of oxygen, just as nitric oxide does to sulphurous acid, during the manufacture of sulphuric acid (406). Another analogous experiment of Traube's consists in heating a solution of cupric oxide containing a large quantity of ammonic chloride with grape sugar: no reduction takes place even when the liquid is boiled; but if a small quantity of reduced and colourless sulphindylic acid be added, the indigo-blue colour reappears, owing to the absorption of oxygen by the sulpho-acid from the cupric oxide; the acid then gives up its oxygen to the sugar, after which it again takes up more oxygen from a fresh quantity of cupric oxide; so that in a short time the whole of the sugar is oxidized, and the cupric oxide reduced to cuprous oxide, whilst the sulphindylic acid is left apparently unaltered. The sulphindylic acid is, in fact, much more easily reduced than cupric oxide, and yet it has the power of easily absorbing oxygen from this oxide. The importance of studying the action of such cases of oxidation must be obvious, when it is borne in mind that it is probably in a great measure by the agency of oxygen that many of the complex substances contained in the animal body are gradually resolved into carbonic anhydride, water, and ammonia.

These slow processes of combustion are intimately connected with the development of ozone. In certain cases the formation of ozone is so abundant during such actions, that they furnish some of the best means of obtaining this singular body. Ozone, for instance, is always formed during the slow oxidation of phosphorus in air; and in the oxidation of oil of turpentine and of ether under particular circumstances, as when a hot platinum wire is suspended in a mixture of the vapour of ether and atmospheric air, a substance is produced which colours a mixture of potassic iodide and starch blue, and also gives a purple colour with chromic acid, similar to that obtained on pouring hydric peroxide into a solution of chromic acid (771). Fudakowski has also shown that phenol, petroleum, and pure benzene, give the same reactions when undergoing slow oxidation at the ordinary temperature.

(1089) *Action of Nascent Hydrogen.*—Although free hydrogen appears to have but little action on carbon compounds, yet in the nascent state it is one of the most important agents, both for ascertaining the nature of the substance under investigation, and also for the synthetical production of new compounds; for this purpose various so-called reducing agents are employed, of which the principal are sodium amalgam in the presence of water, tin and hydrochloric acid, zinc and hydrochloric or sulphuric acid, iron and acetic acid, or ferrous oxide obtained by precipitating a solution of ferrous sulphate with an alkali or alkaline earth. A concentrated aqueous solution of hydriodic acid at a high temperature is one of the most powerful reducing agents known, for although itself stable, yet it is readily decomposed into its constituent elements, hydrogen and iodine, in the presence of compounds which are acted on by nascent hydrogen. The action of sulphuretted hydrogen and ammonic hydric sulphide is somewhat similar, sulphur being deposited in the former case, whilst ammonic disulphide is formed in the latter. A solution of sulphurous acid, H_2SO_3, is also occasionally employed; in the presence of bodies having a strong attraction for hydrogen, water is then decomposed, the liberated oxygen simultaneously combining with a molecule of sulphurous acid to form sulphuric acid:

$$H_2SO_3 + OH_2 = H_2SO_4 + H_2.$$

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The grey coloured powder called "zinc dust" obtained in the manufacture of zinc, and consisting chiefly of that metal in a finely divided state, mixed with some oxide and hydrate, has proved very useful in converting certain oxidized substances into the corresponding hydrocarbon; it was by this means that alizarin was discovered to be a derivative of anthracene.

Hydrogen, like oxygen, varies much in its action on organic bodies.

1. It may combine directly with the carbon compound; for instance, the copper derivative of acetylene, acetylide of copper,

yields ethylene when heated with zinc and dilute ammonia, the acetylene at the moment of its liberation combining with the hydrogen produced by the action of the aqueous ammonia on the zinc:

$$\underset{\text{Acetylene.}}{C_2H_2} + H_2 = \underset{\text{Ethylene.}}{C_2H_4}.$$

Similarly, aldehydes and ketones are converted into alcohols, acetone, for example, yielding isopropylic alcohol:

$$\underset{\text{Acetone.}}{C_3H_6O} + H_2 = \underset{\text{Isopropylic alcohol.}}{C_3H_8O};$$

$$C(CH_3)_2O + H_2 = C(CH_3)_2H.OH;$$

and the nitriles of the acids the corresponding amines:

$$\underset{\text{Acetonitrile.}}{C_2H_3N} + 2H_2 = \underset{\text{Ethylamine.}}{C_2H_7N}.$$

$$C^{iv}(CH_3)'N''' + 2H_2 = C(CH_3)H_2.NH_2.$$

2. Sometimes oxygen appears to be removed by the action of nascent hydrogen, as in the case of malic acid, which by the action of hydriodic acid is converted into succinic acid:

$$\underset{\text{Malic acid.}}{C_4H_6O_5} + H_2 = \underset{\text{Succinic acid.}}{C_4H_6O_4} + OH_2;$$

$$C_2H_3(OH)(COOH)_2 + H_2 = C_2H_4(COOH)_2 + OH_2;$$

or the conversion of lactic acid into propionic acid by similar means:

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} + H_2 = \underset{\text{Propionic acid.}}{C_4H_6O_2} + OH_2.$$

$$C_2H_4(OH).COOH + H_2 = C_2H_5.COOH + OH_2.$$

In these instances, however, the oxygen is not simply removed, but the OH group in the acid is displaced by hydrogen. In all probability the action takes place in two stages, the first being the formation of an iodo-acid:

$$\underset{\text{Lactic acid.}}{C_2H_4(OH).COOH} + HI = \underset{\text{Iodopropionic acid.}}{C_2H_4I.COOH} + OH_2;$$

$$C_2H_4I.COOH + HI = C_2H_5.COOH + I_2.$$

3. It may remove oxygen, or one of the halogens, replacing it by an equivalent quantity of hydrogen. Thus, oxalic acid treated with zinc and dilute sulphuric acid yields glycollic acid:

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} + 2H_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3} + OH_2.$$

$$\left\{\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix}\right. + 2H_2 = \left\{\begin{matrix}\mathrm{CH_2OH}\\ \mathrm{COOH}\end{matrix}\right. + OH_2.$$

Again, the action of hydriodic acid on iodacetic acid regenerates acetic acid:

$$\underset{\text{Iodacetic acid.}}{C_2H_3IO_2} + HI = \underset{\text{Acetic acid.}}{C_2H_4O_2} + I_2.$$

Berthelot (*Ann. Ch. Phys.* [3], li. 48) has pointed out that when the compounds to be acted upon are of a very stable character, *free hydrogen*, at an elevated temperature, may effect this species of substitution, although a good deal of the compound is always destroyed. Several of the chlorides of carbon yield such results; for instance, tetrachlorethylene, C_2Cl_4, when its vapour mixed with hydrogen is passed through a glass tube filled with fragments of pumice and heated to redness, furnishes hydrochloric acid and ethylene or olefiant gas:

$$C_2Cl_4 + 4H_2 = C_2H_4 + 4HCl.$$

Tetrachloromethane or carbonic tetrachloride, CCl_4, yields methane or marsh gas and ethylene:

$$CCl_4 + 4H_2 = CH_4 + 4HCl.$$

The ethylene is the result of the effect of heat upon the carbon tetrachloride, which is partially decomposed into tetrachlorethylene, C_2Cl_4, and free chlorine; and this tetrachlorethylene is then converted into ethylene by the action of the hydrogen, as already explained.

4. When nitro-compounds are treated with reducing agents the oxygen in the NO_2 group is generally replaced by an equal number of atoms of hydrogen, giving rise to corresponding amido-compounds, as in the conversion of nitrobenzene into amido-benzene or aniline:

$$\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + 3H_2 = \underset{\text{Aniline.}}{C_6H_5.NH_2} + 2OH_2.$$

5. Almost all carbon compounds, by treatment at 275° with a large excess of hydriodic acid of density 2·0, are ultimately converted into the corresponding saturated hydrocarbons or paraffins. Thus the oxygen in phenol, C_6H_6O, can be removed, giving rise to benzene, C_6H_6, and this by the continued action of the acid is ultimately converted into hexane or hexylic hydride, C_6H_{14}. In

a similar manner, aldehyde, C_2H_4O, is converted into ethane or ethylic hydride, C_2H_6. Berthelot, by enclosing the bromide of ethylene, of propylene, of butylene, and of amylene, in strong glass tubes with water, copper foil, and potassic iodide, and subsequently heating the mixture to 275° C. (527° F.), in an oil bath, procured ethylene, propylene, butylene, and amylene, accompanied by some gaseous bodies which are products of a secondary decomposition. If the use of copper be omitted, these products of secondary decomposition are more considerable; so that in the latter case it would appear that a part of the organic body had undergone oxidation at the expense of the oxygen of the water, whilst the hydrogen had effected an inverse substitution and formed ethane, propane, tetrane, and pentane. When the copper is present the reaction is probably of the following nature:

$$\underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} + Cu = \underset{\text{Ethylene.}}{C_2H_4} + CuBr_2;$$

and when the copper is not added, the decomposition may be represented as follows:

$$\underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} + 2H_2 = \underset{\text{Ethane}}{C_2H_6} + 2HBr.$$

(1090) *Action of the Halogens upon Organic Compounds—Substitution for Hydrogen.*—The action of chlorine and bromine upon carbon compounds generally gives rise to new ones, in which one or more atoms of the hydrogen in the original substance has been displaced by the halogen. The action of bromine is weaker than that of chlorine, and iodine never produces substitution compounds by its direct action, so that in order to obtain them, it is necessary to have recourse to various indirect methods. The carbon compounds containing fluorine have been but little studied.

Besides the direct action of the element itself other methods for the chlorination of organic bodies are resorted to, such as the employment of iodine trichloride, antimonic pentachloride, phosphoric pentachloride, or potassic chlorate and hydrochloric acid, although in many instances the chlorate simultaneously oxidizes the compound, giving rise to an action of a more complex character.

It is sometimes inconvenient to use the chlorine in the gaseous state, but this difficulty may be obviated by using chlorine hydrate (335), or a saturated solution of chlorine in carbonic tetrachloride. The use of bromine in the presence of iodine bromide, or antimonic pentabromide, is occasionally resorted to when bromine alone does not act.

Some chlorine and bromine substitution compounds yield the corresponding iodine derivatives when treated with potassic iodide. Iodacetic acid is thus obtained from bromacetic acid:

$$\underset{\text{Bromacetic acid.}}{C_2H_3BrO_2} + KI = \underset{\text{Iodacetic acid.}}{C_2H_3IO_2} + KBr.$$

If an organic compound be simultaneously treated with iodine and mercuric or plumbic oxide, the hydriodic acid formed by the union of the iodine with the hydrogen of the carbon compound is at once removed from the sphere of action as mercuric or plumbic iodide:

$$2HI + HgO = HgI_2 + OH_2.$$

Iodic acid may be employed for the same purpose, when water and free iodine will be produced:

$$5HI + HIO_3 = 3OH_2 + 3I_2.$$

If excess of iodic acid be present, the liberated iodine can again react with another portion of the organic compound.

1. The halogens may enter into direct combination with the substance; as when ethylene is converted into ethylenic iodide:

$$\underset{\text{Ethylene.}}{C_2H_4} + I_2 = \underset{\text{Ethylenic iodide.}}{C_2H_4I_2}.$$

or as in the formation of dibromolactic acid from pyruvic acid by the action of bromine:

$$\underset{\text{Pyruvic acid.}}{C_3H_4O_3} + Br_2 = \underset{\text{Dibromolactic acid.}}{C_3H_4Br_2O_3}.$$

2. They may simply remove hydrogen; as in the conversion of alcohol into aldehyde:

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 = \underset{\text{Aldehyde.}}{C_2H_4O} + 2HCl.$$

3. They may act as oxidizing agents by liberating oxygen from water; as when butyric is converted into succinic acid:

$$\underset{\text{Butyric acid.}}{C_4H_8O_2} + 3Br_2 + 2H_2O = \underset{\text{Succinic acid.}}{C_4H_6O_4} + 6HBr.$$

Secondary products, however, accompany this reaction, and a quantity of carbonaceous matter is deposited (Friedel and Machuca).

4. They may produce compounds by substitution, in which

one or more atoms of hydrogen are displaced by chlorine or bromine, while hydrochloric or hydrobromic acid escapes. It is generally advantageous, in conducting this experiment with chlorine, to submit the organic compound to the action of the dry gas: the chlorine is rapidly absorbed, especially if the action be aided by heat or by exposure to the direct rays of the sun, and abundance of hydrochloric acid escapes, and a new body, into the composition of which chlorine enters, is formed. In the majority of cases the new product is analogous to the compound from which it is procured, but a certain number of atoms of the hydrogen has been displaced by a corresponding number of atoms of chlorine. Gay-Lussac, when examining the action of chlorine on wax, was the first to observe this kind of substitution.

A simple case is that of methane or marsh gas, which, when mixed with an equal volume of chlorine and exposed to diffused daylight, has one of its hydrogen atoms displaced by chlorine, monochloromethane or methylic chloride being formed, thus:

$$\underset{\text{Methane.}}{CH_4} + Cl_2 = \underset{\text{Monochlormethane.}}{CH_3Cl} + HCl.$$

By the further action of chlorine a second atom of hydrogen is displaced, and dichloromethane or methylenic chloride is produced:

$$\underset{\text{Monochloromethane.}}{CH_3Cl} + Cl_2 = \underset{\text{Dichloromethane.}}{CH_2Cl_2} + HCl.$$

This compound is then readily converted into trichloromethane or chloroform, thus:

$$\underset{\text{Dichloromethane.}}{CH_2Cl_2} + Cl_2 = \underset{\text{Trichloromethane.}}{CHCl_3} + HCl.$$

And finally, the chloroform, when submitted to the action of chlorine whilst exposed to bright sunlight, or when heated with antimonic pentachloride, has the last atom of hydrogen displaced by chlorine with formation of tetrachloromethane or carbonic tetrachloride:

$$\underset{\text{Trichloromethane.}}{CHCl_3} + Cl_2 = \underset{\text{Tetrachloromethane.}}{CCl_4} + HCl.$$

The discovery that the substitution of chlorine for hydrogen was practicable, at first excited the greatest astonishment amongst chemists, since owing to the powerful attractions of chlorine, particularly when its electrical opposition to hydrogen is borne in mind, the possibility of such an occurrence had never been suspected. The displacement of oxygen by chlorine was familiar to the mind of the chemist, but the displacement of hydrogen by chlorine was a circumstance entirely in opposition to the doctrines of chemical attraction then prevalent. The discovery of this remarkable fact has led to the production of an immense number of substitution compounds. The new products so obtained are in general possessed of comparatively little intrinsic interest. The importance of accurately studying the steps by which these substitutions are effected, can, however, be scarcely over-estimated, owing to the light which they frequently throw upon the constitution of the different compounds, and of their relations to others where no obvious connexion had been previously traced. The first atoms of hydrogen are usually displaced more readily than the others. It is often necessary at first to moderate the action by cooling the liquid artificially, and by placing it either in obscurity or only in the diffused light of day; while to complete the displacement of the last portions, the strongest sunlight, aided by a temperature of ebullition, is frequently requisite.

Substitutions of bromine for hydrogen may also be effected by analogous methods, although, owing to its feebler chemical attractions, the reactions ordinarily take place with less vehemence.

(1091) *Haloid Compounds of Phosphorus.*—Closely allied to the action of the halogens is that of the haloid compounds of phosphorus, namely, phosphoric chloride and oxychloride, phosphorous chloride, and the corresponding bromine and iodine compounds.

1. The action upon acids and other compounds containing the OH group is generally to displace the OH group by the halogen; thus phosphoric chloride, phosphoric oxychloride, and phosphorous chloride, all produce acetic chloride by their action on acetic acid:

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + PCl_5 = \underset{\text{Acetic chloride.}}{C_2H_3OCl} + POCl_3 + HCl.$$

$$CH_3.CO(OH) + PCl_3 = CH_3.COCl + POCl_3 + HCl.$$

$$\underset{\text{Acetic acid.}}{3C_2H_4O_2} + PCl_3 = \underset{\text{Acetic chloride.}}{3C_2H_3OCl} + H_3PO_3.$$

$$3C_2H_4O_2 + POCl_3 = 3C_2H_3OCl + H_3PO_4.$$

2. In some cases oxygen is removed and displaced by chlorine, as when aldehyde is treated with phosphoric chloride:

$$\underset{\text{Aldehyde.}}{C_2H_4O} + PCl_5 = \underset{\text{Ethylidenic chloride.}}{C_2H_4Cl_2} + POCl_3.$$

(1092) *Action of Hydrochloric, Hydrobromic, and Hydriodic Acids.*—These, like other acids, unite directly with the various organic substances of a basic nature, forming salts or compounds analogous to them, and hydriodic acid, as previously mentioned (1089), is a powerful reducing agent. Besides these, however, the haloid acids have other modes of action.

1. They combine directly with certain unsaturated compounds; thus hydriodic acid and ethylene combine and form moniodethane or ethylic iodide:

$$\underset{\text{Ethylene.}}{C_2H_4} + HI = \underset{\text{Ethylic iodide.}}{C_2H_5I};$$

and fumaric acid, when treated with hydrobromic acid, yields bromosuccinic acid:

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + HBr = \underset{\text{Bromosuccinic acid.}}{C_4H_5BrO_4}.$$

2. The OH group in the alcohols and oxy-acids is displaced by the halogen of the haloid acid; for instance, the action of hydrochloric acid on alcohol gives rise to ethylic chloride:

$$\underset{\text{Alcohol.}}{C_2H_5.OH} + HCl = \underset{\text{Ethylic chloride.}}{C_2H_5Cl} + OH_2;$$

and malic acid, when heated with hydrobromic acid, is converted into monobromosuccinic acid:

$$\underset{\text{Malic acid.}}{C_2H_3.OH(COOH)_2} + HBr = \underset{\text{Bromosuccinic acid.}}{C_2H_3Br(COOH)_2} + OH_2.$$

(1093) *Action of Nitric Acid and of Nitrous Acid.*—From the readiness with which it parts with its oxygen, nitric acid, as already noticed, is a most powerful oxidizing agent, and, like other acids, it also combines with carbon compounds of a basic nature. In addition to these modes of action there are others which are of considerable importance in the investigation of the nature of organic substances.

1. The H in the OH group in the alcohols may be displaced by NO_2, giving rise to nitric ethers. In this manner ethylic nitrate is formed from alcohol:

$$\underset{\text{Alcohol.}}{C_2H_5(OH)} + HNO_3 = \underset{\text{Ethylic nitrate.}}{C_2H_5(NO_3)} + OH_2;$$

and so-called nitroglycerin from glycerin:

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + 3HNO_3 = \underset{\text{Nitroglycerin.}}{C_3H_5(NO_3)_3} + 3OH_2.$$

2. One or more atoms of hydrogen are displaced by an equal number of NO_2 groups with simultaneous elimination of water. A nitro-substitution compound is thus formed, as in the preparation of nitrobenzene from benzene by the action of concentrated nitric acid:

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + OH_2.$$

When a mixture of sulphuric and nitric acids is employed two atoms of hydrogen are displaced and dinitrobenzene is produced:

$$\underset{\text{Benzene.}}{C_6H_6} + 2HNO_3 = \underset{\text{Dinitrobenzene.}}{C_6H_5(NO_2)_2} + 2OH_2.$$

As a rule, the latter class, the nitro-compounds, are far more stable than the nitric ethers, and far less explosive. Most nitro-compounds are readily reduced by the action of nascent hydrogen with formation of amido-derivatives, differing from the original compound in having one or more of the NO_2 groups displaced by NH_2. In this way aniline is obtained from nitrobenzene. On the other hand, the nitric ethers when treated with reducing agents furnish the alcohol from which they were derived.

3. The action of nitrous acid on the amido-compounds frequently gives rise to a very remarkable class of substances, termed azo-derivatives. Thus, by the action of nitrous acid on aniline nitrate, diazobenzene nitrate is produced:

$$\underset{\text{Aniline nitrate.}}{(C_6H_5)H_3N.NO_3} + HNO_2 = \underset{\text{Diazobenzene nitrate.}}{(C_6H_5)N_2.NO_3} + 2OH_2.$$

4. Many amido-compounds, when treated with nitrous acid, yield the corresponding alcohol with simultaneous evolution of nitrogen. The best result is usually obtained by the action of argentic nitrite on the hydrochloride of the base. For example, alcohol may be obtained from ethylamine in this way:

$$\underset{\substack{\text{Ethylamine}\\ \text{hydrochloride.}}}{(C_2H_5)NH_3Cl} + AgNO_2 = \underset{\text{Alcohol.}}{C_2H_5(OH)} + AgCl + OH_2 + N_2.$$

(1094) *Dehydrating Agents.*—Phosphoric anhydride, phosphoric sulphide (pentasulphide), potassic hydric sulphate, zincic chloride, and hydrochloric acid, when heated with organic compounds containing oxygen, may remove the elements of water. This action frequently gives rise at the same time to a more extended decomposition, and the substance splits up, yielding several products. Zincic chloride also possesses the peculiar property of polymerizing many hydrocarbons at the instant of their formation from oxidized bodies by this means. Moreover, sulphuric acid, at a high temperature, acts as a powerful oxidizing agent, and phosphoric sulphide frequently removes oxygen and displaces it by sulphur. The great variation in the modes of action thus introduced renders it impossible to describe all of them here, and they will therefore be treated of from time to time as the particular cases come into notice. In the meantime some of the simpler cases of dehydration are here given.

1. When sulphuric acid removes the elements of water from oxalic acid it splits up into carbonic anhydride and carbonic oxide:

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} - \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{CO.}$$

2. Crotonic aldehyde is formed from ordinary acetic aldehyde when it is heated with zincic chloride:

$$\underset{\text{Aldehyde.}}{2C_2H_4O} = \underset{\text{Crotonic aldehyde.}}{C_4H_6O} + OH_2.$$

3. When glycerin is heated with hydric potassic sulphate the elements of water are removed, and acroleïn is produced:

$$\underset{\text{Glycerin.}}{C_3H_8O_3} - 2OH_2 = \underset{\text{Acroleïn.}}{C_3H_4O.}$$

4. Camphor, when distilled with zincic chloride, phosphoric anhydride, or phosphoric sulphide, loses the elements of water, and becomes converted into cymene:

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} - OH_2 = \underset{\text{Cymene.}}{C_{10}H_{14}.}$$

5. On allowing a mixture of amylic alcohol with zincic chloride to stand for some time, and then distilling, amylene is obtained:

$$\underset{\text{Amylic alcohol.}}{C_5H_{12}O} = \underset{\text{Amylene.}}{C_5H_{10}} + OH_2.$$

Much of the amylene, however, becomes polymerized at the moment of formation by the action of the zincic chloride, so that the amylene is always mixed with diamylene, $C_{10}H_{20}$, triamylene, $C_{15}H_{30}$, tetramylene, $C_{20}H_{24}$, &c.

(1095) *Alkaline Reagents.*—The action of potassic and sodic hydrates, and of baryta and lime, both caustic and hydrated, may here be considered. Besides forming salts with the various organic acids, they give rise to reactions of some importance in the experimental investigation of the nature of the carbon compounds.

1. Fused potassic and sodic hydrates often act as powerful oxidizing agents, but as hydrogen is always evolved in this case, the results are frequently complicated from an oxidizing and reducing action going on simultaneously. A simple instance is the conversion of amylic alcohol into valerianic acid by the action of hot soda-lime:

$$\underset{\text{Amylic alcohol.}}{C_5H_{12}O} + O_2 = \underset{\text{Valerianic acid.}}{C_5H_{10}O_2} + OH_2.$$

In a similar manner cellulose is oxidized to oxalic acid. Advantage has been taken of this for the preparation of the acid on a large scale by the treatment of sawdust with a mixture of potassic and sodic hydrates.

2. The elements of hydrochloric acid are removed from chlorine compounds by the action of the alkali; thus ethylenic chloride, when treated with an alcoholic solution of potassic hydrate, yields monochlorethylene or vinylic chloride:

$$\underset{\text{Ethylenic chloride.}}{C_2H_4Cl_2} - HCl = \underset{\text{Vinylic chloride.}}{C_2H_3Cl}.$$

Many bromine and iodine compounds behave in a similar way; for instance, the vapour of vinylic bromide, when passed into a hot alcoholic solution of potassic hydrate, yields acetylene:

$$\underset{\text{Vinylic bromide.}}{C_2H_3Br} - HBr = \underset{\text{Acetylene.}}{C_2H_2}.$$

3. Many acids when heated with lime, or with soda-lime, are decomposed with elimination of carbonic anhydride, which forms a carbonate with the alkali, or the alkaline earth; thus a mixture of sodic acetate with twice its weight of soda-lime, under these circumstances, yields methane or marsh-gas:

$$\underset{\text{Sodic acetate.}}{C_2H_3NaO_2} + \underset{\text{Sodic hydrate.}}{ONaH} = \underset{\text{Methane.}}{CH_4} + \underset{\text{Sodic carbonate.}}{CO_3Na_2}.$$

$$CH_3.COONa + ONaH = CH_4 + CO(ONa)_2.$$

In like manner, phthalic acid splits up into benzene and carbonic anhydride:

$$\underset{\text{Phthalic acid.}}{C_8H_6O_4} = \underset{\text{Benzene.}}{C_6H_6} + 2CO_2.$$

4. The HSO_3 group in the sulphonic acids is displaced by the group OH when their salts are fused with potassic or sodic hydrates, as is the case with potassic benzenesulphonate:

$$\underset{\text{Potassic benzenesulphonate.}}{C_6H_5(KSO_3)} + 2KHO = \underset{\text{Potassic phenate.}}{C_6H_5.OK} + SO_3K_2 + OH_2.$$

On dissolving the product in water, and acidulating with an acid, the potassic phenate is decomposed and phenol (C_6H_5OH) liberated, which differs from benzenesulphonic acid, $C_6H_5(HSO_3)$, in containing hydroxyl in place of the HSO_3 group.

(1096) *Use of Acetic Chloride and Benzoic Chloride.*—These compounds are of considerable importance in examining the constitution of certain organic compounds containing oxygen, for by their means we can, in most cases, determine with certainty the number of OH groups there are in the substance. These chlorides react with the oxygen compounds in such a manner that the hydrogen in the OH groups is displaced by acetyl or benzoyl respectively, according to the chloride which has been employed; for instance, acetic acid, when treated with acetic chloride gives rise to acetic acetate or acetic anhydride:

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + \underset{\text{Acetic chloride}}{C_2H_3OCl} = \underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} + HCl.$$

Again, orcin, $C_7H_8O_2$, is thus shown to contain two OH groups, and to be, therefore, a dihydroxyl derivative of toluene, $C_7H_6(OH)_2$. The action is as follows:

$$\underset{\text{Orcin.}}{C_7H_6(OH)_2} + \underset{\text{Benzoic chloride.}}{2C_7H_5OCl} = \underset{\text{Dibenzoyl-orcin.}}{C_7H_6O_2(C_7H_5O)_2} + 2HCl.$$

(1097) The list of reagents, the use of which has been considered in the preceding paragraphs, is far from being exhaustive, although it includes most of those which are of general application. The others, such as ammonia, cyanogen, &c., usually give rise to a special class of reactions, which will be most conveniently studied when describing the compounds produced in this way.

Amongst those forces which affect chemical reactions the one brought most prominently under the notice of the chemist is undoubtedly heat. Some organic substances, and especially those of complex structure, split up into compounds of a simpler nature when subjected to a high temperature. In other cases the union of two organic compounds, or the action of reagents on them, is greatly facilitated by gently heating them. The variations in chemical action caused by elevations of temperature are so numerous, and of such universal occurrence, that the effects produced by it must, of necessity, be considered when the formation and preparation of the individual compounds are described.

The effect of insolation, or exposure to the direct rays of the sun, is in many instances very marked, as has already been noticed in the formation of hydrochloric acid from hydrogen and chlorine (336). Results of a similar nature are frequently obtained with organic compounds; for instance, mercury has no perceptible action on methylic iodide when protected from the light, but on exposure to the direct solar rays combination gradually ensues, and mercuric iodomethide, $HgCH_3I$, is produced.

CHAPTER IV.

CYANOGEN AND ITS COMPOUNDS.

(1098) Cyanogen: C_2N_2 or $Cy_2=52$.—This substance is one of the most interesting compounds of carbon, and its discovery by Gay-Lussac, in 1814, formed an epoch in the history of chemical science. It was the first compound body which was distinctly proved to enter into reactions in a manner similar to that in which the elements do. New views of chemical composition were thus originated, which were afterwards extensively developed in the theory of the so-called compound radicles, and have exercised a most material inflence upon the theory of organic compounds in general. The name of *Cyanogen* (from *κύανος* blue, *γεννάω* to produce), is derived from the circumstance that this body forms an essential ingredient in Prussian blue. It does not as yet seem to have been formed by the direct union of its constituent elements, but if a mixture of charcoal and potassic carbonate be heated to redness in a porcelain tube, and nitrogen passed over it, carbonic oxide escapes abundantly, whilst potassic cyanide is produced: $K_2CO_3+4C+N_2=2KCN+3CO$. This operation takes place in the blast furnace during the smelting of iron, a notable quantity of potassic cyanide being formed near the hottest part (*note*, 730), the potassium being derived from the ashes of the coal or from the clay in the ore employed.

Ammonia if passed over glowing charcoal yields cyanogen compounds still more readily, especially when potassic carbonate is also present. The oxidized compounds of nitrogen, such as the nitrates, likewise readily furnish small quantities of the compounds of cyanogen, as is frequently observed in deflagrating charcoal with nitre.

The sensitive reaction for ascertaining the presence of nitrogen in organic compounds already mentioned (1036) is founded upon the facility with which either potassium or sodium determines the formation of cyanogen from nitrogenized compounds of carbon. Advantage is also taken of this circumstance in the manufacture of potassic ferrocyanide. When animal matters containing nitrogen are heated with potassic carbonate at a high temperature, the latter is reduced, and the potassium at the moment of its liberation combines with the nitrogen and a portion of the carbon to form potassic cyanide, which is subsequently converted into ferrocyanide (1114).

Cyanogen is also present in small quantity among the products obtained during the distillation of pit coal, and it is formed during the decomposition of ammonic oxalate by heat, $C_2O_4(NH_4)_2$ yielding $C_2N_2+4OH_2$.

Cyanogen is usually prepared by strongly heating dry mercuric cyanide, $HgCy_2$, in a retort or glass tube, when it splits up into metallic mercury and cyanogen gas which should be collected over mercury. Instead of mercuric cyanide a mixture of two parts of thoroughly dried potassic ferrocyanide and three of mercuric chloride may be employed.

Cyanogen is a transparent colourless gas which burns with a beautiful rose-edged purple flame. It has a peculiar penetrating odour and is poisonous if respired. Water at the ordinary temperature dissolves about four times its volume of the gas, and it is still more freely soluble in alcohol. In porcelain or glass vessels it supports a high temperature without decomposition, but if heated in iron tubes, charcoal is deposited, and a volume of nitrogen remains equal to that of the cyanogen used.

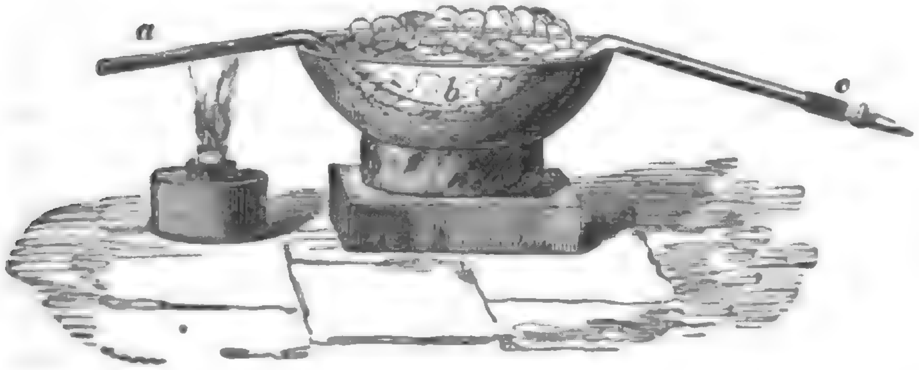
The composition of cyanogen may be determined by detonation in the eudiometer with oxygen, the combustion being attended with a powerful explosion. One volume of cyanogen and two volumes of oxygen yield two of carbonic anhydride and one of nitrogen: $C_2N_2+2O_2=2CO_2+N_2$; two volumes of cyanogen therefore contain two volumes of nitrogen, or 28 parts by weight, united to 24 parts by weight of carbon:

			By weight.			By vol.
Carbon ...	C_2	=	24	or 46·15	...	?
Nitrogen ...	N_2	=	28	53·85	...	2
Cyanogen ...	C_2N_2	=	52	100·00	...	2

Cyanogen is readily reduced to the liquid state by a pressure of about four atmospheres at a temperature of $-12^\circ\cdot5$ ($9^\circ\cdot5$ F.). It forms a colourless, limpid liquid, of sp. gr. 0·866 at 17° ($62^\circ\cdot6$ F.), which, on the removal of the pressure, rapidly but quietly resumes the gaseous state; according to Bunsen it boils at $-20^\circ\cdot7$ (-5° F.). It freezes at $-34^\circ\cdot5$ (-30° F.), and forms a transparent crystalline solid, which is nearly of the same density as the liquid.

Fig. 390 shows an easy method of liquefying cyanogen by the pressure of its own vapour: a tube of hard glass is bent in the form of *a*, *b*, *c*. Into the limb, *a*, well-dried mercuric cyanide is introduced; the bend, *b*, is placed in a basin containing a freezing mixture of ice and salt, and heat is applied cautiously to the cyanide at *a*; as soon as the gas begins to escape, the stopcock at *c* is closed, and the cyanogen then becomes condensed in the liquid state and collects in the bend, *b*.

FIG. 390.



If potassium be heated in cyanogen it burns and combines with it, forming potassic cyanide, a saline body analogous to sodic chloride or common salt: $C_2N_2 + K_2 = 2KCN$. This reaction is evidently analogous to that which takes place with chlorine and potassium under similar circumstances: $Cl_2 + K_2 = 2KCl$, and serves to illustrate the existence of the remarkable property possessed by cyanogen of behaving with metals and other bodies like the haloid elements. The aqueous solution of cyanogen gradually decomposes when kept; a brown substance is deposited, and the solution contains ammonic oxalate together with other products: $C_2N_2 + 4OH_2 = C_2O_4(NH_4)_2$. When cyanogen is passed into a concentrated solution of hydrochloric acid the liquid after some hours deposits crystal of *oxamide*: $C_2N_2 + 2OH_2 = C_2O_2(NH_2)_2$. Dry ammonia and cyanogen combine, forming *hydrazulmin*, $C_4N_6H_6$ (see mycomelic acid).

(1099) PARACYANOGEN, C_xN_x.—When thoroughly dry mercuric cyanide is strongly heated, as in the preparation of cyanogen, a brown residue is left in the retort, which consists of a compound of carbon and nitrogen of the same centesimal composition as cyanogen. The constitution of *paracyanogen*, as this polymeride of cyanogen is called, is at present unknown. According to Troost and Hautefeuille, the best method of preparing it is to heat the dry mercuric cyanide in sealed tubes to 440° (824° F.) in boiling sulphur for twenty-four hours, subsequently removing the mercury by heating the product to 440° (824° F.) in a stream of cyanogen; by this means 40 per cent. of the cyanogen present is converted into paracyanogen (*Comptes rendus*, lxvi. 735, 795). Argentic cyanide also, when strongly heated under pressure, yields a large proportion of paracyanogen. This compound is insoluble in water, and is neither volatile nor fusible. When heated to 860° (1580° F.), it is entirely reconverted into gaseous cyanogen.

(1100) HYDROCYANIC ACID; *Hydric Cyanide, or Prussic Acid:* HCN or $HCy = 27$.—When a mixture of cyanogen and hydrogen is submitted to the action of the silent electric discharge the two gases unite to form the so-called hydrocyanic acid, but other substances appear to be produced at the same time: $C_2N_2 + H_2 = 2HCN$; it has also been observed by Berthelot that when a rapid stream of sparks from an induction coil is passed through a mixture of acetylene and nitrogen a portion of the mixed gases is converted into hydrocyanic acid: $C_2H_2 + N_2 = 2HCN$. Hydrocyanic acid, mixed with a peculiar essential oil, is obtained by distillation from the kernels of the bitter almond, and from those of many varieties of stone fruit; it is also present in the water which is distilled off the leaves of the laurel, the peach, and some other shrubs; the juice of the tapioca plant (*Jatropha manihot*) likewise contains it, and it is also formed under various circumstances during the oxidation and decomposition of certain nitrogenized substances.

The acid may be easily prepared in many ways; thus, if a current of dried sulphuretted hydrogen be passed through a long tube filled with mercuric cyanide until the latter has become almost entirely blackened, mercuric sulphide and hydrocyanic acid are formed: $HgCy_2 + H_2S = HgS + 2HCy$. It may also be obtained by decomposing any of the cyanides with a strong acid, and subjecting them to distillation; for example, mercuric cyanide when treated with hydrochloric acid yields it readily, but as hydrocyanic acid combines with the mercuric chloride formed during the reaction, the whole of the hydrocyanic acid is not obtained by this means unless ammonic chloride be added to the mixture: this combines with the mercuric chloride and liberates the hydrocyanic acid. The most economical process is that of Wöhler: he prepares a crude potassic cyanide by fusing 8 parts of dried potassic ferrocyanide with 3 of potassic carbonate and 1 part of charcoal. The decomposition which takes place is shown in the following equation: $K_4FeCy_6 + K_2CO_3 + 2C = 6KCy + Fe + 3CO$. The fused mass is treated with 6 times its weight of water, in a well-closed vessel, and the clear liquid, decanted from the iron which it is the object of this operation to separate, is poured into a retort; sulphuric acid, diluted with an equal weight of water, is then gradually added in the proportion of 1 part of the acid to 2 of the cyanide. At first the distillation proceeds spontaneously from the heat developed by the admixture of the sulphuric acid with the water, and in order to condense the acid, the products are made to pass through a long U-shaped tube, immersed in cold water, and filled with calcic chloride, with the exception of the first fourth of the tube, which contains fragments of the crude potassic cyanide; to the bent tube is attached a second delivering tube, which passes to the bottom of a bottle cooled with ice and salt. The calcic chloride in the U-tube retains the moisture, and the potassic cyanide any sulphuric acid that might chance to pass over, whilst the hydrocyanic acid collects in the anhydrous state in the cooled receiver. Owing to its intensely poisonous character, and almost instantaneous action in destroying life, the greatest care is requisite in conducting experiments with this substance; the apparatus should always be arranged so that the vapours are carried away from the operator by a brisk current of air. The reaction of sulphuric acid upon potassic cyanide is very simple, being exactly analogous to its action upon sodic chloride:

$$2KCy + 2H_2SO_4 = 2HCy + 2KHSO_4.$$

Anhydrous hydrocyanic acid is a colourless, transparent liquid, which boils at 26°·5 (80° F.); sp. gr. ·7058 at 7° (44°·6 F.) It is very volatile; in fact, so rapidly does it evaporate, that if a drop be allowed to fall upon a glass plate, part of the acid becomes frozen by the cold produced by its own evaporation. Its vapour has an odour resembling that of peach blossoms, causing a peculiar sense of oppression, and a constriction in the fauces.

Hydrocyanic acid is very inflammable; it burns with a flame resembling that of cyanogen, but of a whiter colour. When potassium is heated in hydrocyanic acid vapour, potassic cyanide is formed, and a volume of hydrogen equal to half that of the vapour employed is liberated; chlorine and bromine decompose it immediately, hydrochloric or hydrobromic acid is produced, and if excess of the halogen be present, cyanogen chloride or bromide is formed. If 5 volumes of oxygen be mingled with

4 of hydrocyanic vapour, a mixture is obtained which detonates powerfully on passing the electric spark; 4 volumes of carbonic anhydride and 2 of nitrogen remain, and 2 volumes of steam are condensed: $4HCN + 5O_2 = 4CO_2 + 2N_2 + 2OH_2$. The composition of hydrocyanic acid may be calculated from the result of this experiment, and may be represented as follows:

				By weight.		By vol.
Carbon	C	=	12	or 44·45	...	?
Nitrogen	N	=	14	51·85	...	1
Hydrogen	H	=	1	3·70	...	1
Hydrocyanic acid ...	HCN	=	27	100·00	...	2

When anhydrous hydrocyanic acid is mixed with its own weight of water, a contraction in bulk amounting to between 6 and 7 per cent. takes place, and at the same time a depression of several degrees of temperature occurs (Bussy and Buignet). The same effects are observed in a smaller degree if the two liquids are mixed in other proportions; but the maximum reduction of temperature occurs when equal weights of the two, corresponding to $2HCy,3OH_2$ are taken. (*Ann. Chim. Phys.* [4], iii. 237.)

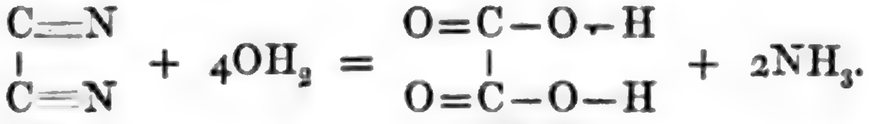
Hydrocyanic acid reddens litmus slightly, dissolves mercuric oxide freely, and precipitates argentic nitrate in white flocculi of argentic cyanide, AgCy; but the acid properties of this body are far less pronounced than those of hydrochloric acid, to which it is analogous in composition, which may be due to cyanogen being but feebly negative as compared with chlorine.

Pure hydrocyanic acid may be kept unchanged according to Gautier, but if it contain a trace of water or ammonic cyanide, or other impurity, it soon alters, especially if exposed to light; a brown humus-like matter is then formed.

Pelouze has pointed out a remarkable decomposition which furnishes dilute hydrocyanic acid almost in a state of purity: 1 molecule of crystallized ammonic formate contains the elements of 1 molecule of hydrocyanic acid and 2 molecules of water. If this salt be placed in a retort and heated, it melts at 120° (248° F.), loses a little ammonia at 140° (284° F.), and between 180° and 200° (356° and 392° F.), distils over; if the vapour be passed through a red-hot tube it is wholly converted into hydrocyanic acid and water: $HCOONH_4 = HCN + 2OH_2$. On the other hand, an aqueous solution of hydrocyanic acid undergoes spontaneous decomposition, part of it being converted into ammonic formate:

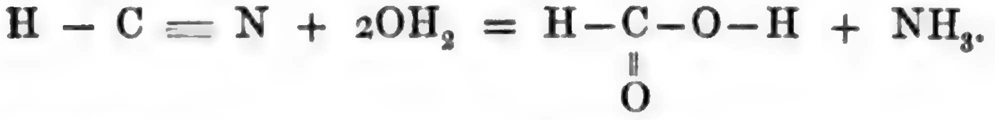
$$HCN + 2OH_2 = HCOONH_4.$$

The formation of oxalic acid from cyanogen (p. 89), and of formic acid from hydrocyanic acid, by the action of water is the result of the conversion of the CN group into the COOH or carboxyl group; thus:



$$\begin{array}{c} C\equiv N \\ | \\ C\equiv N \end{array} + 4OH_2 = \begin{array}{c} O=C-O-H \\ | \\ O=C-O-H \end{array} + 2NH_3.$$

Cyanogen. Oxalic acid.



$$H-C\equiv N + 2OH_2 = H-\underset{\overset{\|}{O}}{C}-O-H + NH_3.$$

Hydrocyanic acid. Formic acid.

This observation is of considerable importance, as, in fact, whenever the $-C\equiv N$ group is present in a compound it may be resolved into the $O=\underset{|}{C}-O-H$ group by the action of water.

Dilute hydrocyanic acid may be prepared by the distillation of potassic ferrocyanide with dilute sulphuric acid; 10 parts of the salt being dissolved in 4 times its weight of warm water, and distilled with 7 parts of the acid diluted with twice its weight of water, until about half the bulk of the liquid has passed over. In this reaction,

$$2K_4(FeCy_6)+6H_2SO_4=6HCy+K_2Fe''(FeCy_6)+6KHSO_4,$$

only one-half of the cyanogen present in the ferrocyanide is obtained as hydrocyanic acid, a white insoluble compound, long known as Everitt's salt, being left in the retort; this has the composition $K_2Fe''(FeCy_6)$, and appears to be identical with the potassic ferrous ferrocyanide formed on adding a solution of a ferrous salt to one of ferrocyanide (1120).

As the acid is now frequently employed in medicine, it is highly important, on account of its energetic action, to be able to insure its preparation of an uniform strength; this is easily attained by the process of a former Pharmacopœia, which directs 48½ grains of argentic cyanide to be suspended in an ounce of water, and to be decomposed by 39½ grains of hydrochloric acid, decanting the clear liquid from the argentic chloride; this acid contains 2 per cent. of the anhydrous acid. The acid when dilute is less prone to decomposition than when concentrated, especially if a little free sulphuric acid be present: but it should always be excluded from the light. This acid is extremely volatile, and if a bottle containing the diluted acid be left open for a few hours it will be found to have suffered a very material reduction in strength; indeed, the mere opening and closing the bottle in dispensing the medicine always reduces its strength. When subjected to distillation a large quantity is usually lost, and the greater portion of the acid comes over in the first fourth of the distillate. What is called *Scheele's acid* varies greatly in strength, owing to the difficulty of condensing the acid vapour. It is directed to be prepared by mixing 10 parts of potassic ferrocyanide with 3·75 of sulphuric acid previously diluted with 40 parts of water, and distilling over till 10 parts are collected. It seldom contains more than 5 per cent. of the acid, and the proportion is often considerably less.

(1101) Hydrocyanic acid possesses the property of combining directly with the haloid acids forming crystalline compounds which in contact with water decompose with the greatest readiness into the corresponding ammonic salt and formic acid, thus:

$$N(CH)'''HCl + 2OH_2 = NH_4Cl + HCOOH.$$

FORMONITRILE HYDROCHLORIDE, or *Methenylammonic Chloride*; $N(CH)'''HCl = HCN,HCl$.—Hydrochloric acid is rapidly absorbed by well cooled anhydrous hydrocyanic acid, and on allowing the mixture to stand it becomes hot and deposits the new compound in a crystalline state. It is very hygroscopic and its solution rapidly decomposes. It is insoluble in ether, but soluble in alcohol, and is decomposed by it. Hydrocyanic acid unites with hydriodic acid to form the hydriodide, CHN,HI. The compound of hydrocyanic acid with hydrobromic acid, according to Gal, has the formula CHN,HBr, but according to Gautier its formula is $2CHN,3HBr$. Compounds of hydrocyanic acid with certain metallic chlorides also exist, such as those with antimonic chloride, $SbCl_5,3HCy$, with ferric chloride $Fe_2Cl_6,4HCy$, and with stannic chloride $SnCl_4,HCy$; they are crystalline substances, and may be prepared by the direct union of hydrocyanic acid with the anhydrous metallic chloride.

(1102) TRIHYDROCYANIC ACID, $C_3N_3H_3$.—When hydrocyanic acid or its aqueous solution is heated with epichlorhydrin, or when an aqueous solution, to which a small quantity of an alkaline hydrate has been added, is allowed to stand for some weeks, a part of the hydrocyanic acid is converted into a polymeric modification, which may be extracted from the brown humus-like mass by means of ether. On evaporating the ethereal solution a brown crystalline mass of the so-called trihydrocyanic acid is left, which can be purified by treatment with animal charcoal and crystallization from hot water. It is only slightly soluble in cold water, more readily in hot water. This compound is decomposed by the action of alkalies or acids, yielding amidoacetic acid or glycocine, carbonic anhydride, and ammonia:

$$\underset{\text{Trihydrocyanic acid.}}{C_3N_3H_3} + 2HCl + 4OH_2 = \underset{\text{Amidoacetic acid.}}{C_2NH_5O_2} + CO_2 + 2NH_4Cl.$$

(1103) *Detection of Hydrocyanic Acid and the Cyanides.*—The presence of hydrocyanic acid or of the soluble cyanides in solution may be determined by the following tests:—

1. With argentic nitrate, a white curdy precipitate is formed, which does not blacken by exposure to light, and is nearly

insoluble in cold nitric acid; when the dry precipitate is heated to redness it gives off cyanogen.—2. If to the liquid a slight excess of potassic hydrate be added, and then a mixture of ferrous and ferric sulphate, a precipitate of hydrated ferric and ferrous oxide is produced, which, when treated with excess of hydrochloric acid, leaves Prussian blue. This test may be modified by gently heating the suspected mixture with sulphuric acid, and suspending in the flask or retort for a few minutes a piece of paper moistened with a solution of potassic hydrate; on dropping a weak solution of the mixed sulphates of iron upon the paper, and then immersing it in diluted sulphuric acid, hydrocyanic acid may be recognised by the formation of Prussian blue when very minute traces only are present.—3. Let the liquid be acidulated with a few drops of hydrochloric acid, place it in a watch-glass, and let a second watch-glass be inverted over it, moistened with a drop of a solution of yellow ammonic sulphide (containing ammonic disulphide); after a few minutes let the upper watch-glass be removed, and the liquid be evaporated to dryness at a gentle heat: ammonic sulphocyanate will be left, and the volatile ammonic sulphydrate will pass off: $(NH_4)_2S_2 + HCN = CNS.NH_4 + SH.NH_4$. On adding a drop of a weak solution of ferric chloride to the dry residue a red colour is produced, due to ferric sulphocyanate.

(1104) *Estimation of Hydrocyanic Acid.*—Liebig has given a ready method for the exact determination of the strength of a solution of hydrocyanic acid founded upon the solubility of the double cyanide of potassium and silver (1109).

The acid to be tested is supersaturated with a solution of potassic hydrate, and a standard solution of argentic nitrate (containing 1·7 gramme of nitrate in 100 cubic centim. of water) is gradually added, agitating the mixture after each addition: as soon as the precipitate is no longer redissolved, the number of cubic centims. of nitrate added is read off; 1·7 grm. of argentic nitrate represent 0·34 grm. of hydrocyanic acid. The reaction is the following: $AgNO_3 + 2KCy = AgCy,KCy + KNO_3$. The presence of chlorides does not interfere with the application of the test.

Cupric sulphate may be substituted for the argentic nitrate if the hydrocyanic solution be rendered alkaline with ammonia instead of with potassic hydrate. The reaction is complete as soon as the liquid acquires a slightly blue tinge: 1·247 grm. of the crystallized sulphate represents 0·54 grm. of hydrocyanic acid.

The quantity of cyanogen in the simple cyanides may be determined by the following method proposed by Heisch (*Journ. Chem. Soc.*, ii. 219). The substance for analysis is placed in a small flask with some pieces of pure zinc and a little water; the neck of the flask is fitted with a cork, through which are passed a tube bent twice at right angles for carrying off the gas which is disengaged, and a tube funnel, down which sulphuric acid is poured. Hydrogen is liberated, and carries off the whole of the cyanogen, in the form of hydrocyanic acid, which is arrested by causing it to pass through a solution of argentic nitrate. The argentic cyanide may afterwards be collected upon a filter and weighed; but it is better to conduct the vapours of hydrocyanic acid into a solution of potassic hydrate, and afterwards to add to the alkaline liquid a standard solution of argentic nitrate, or of cupric sulphate.

(1105) CYANIDES.—The cyanides of the metals of the alkalies and alkaline earths are freely soluble in water, whilst most of the cyanides of the heavy metals are insoluble; when boiled with hydrochloric acid they are generally decomposed with evolution of hydrocyanic acid; those of silver and mercury, when heated to redness, yield cyanogen gas. The soluble cyanides give a grey precipitate of the reduced metal when mixed with a solution of a mercurous salt; the mercuric salts, on the contrary, give no precipitate. Most of the cyanides which are insoluble in water may be dissolved by means of a solution of the cyanide of an alkali metal: in such cases double cyanides are generally formed. The cyanides of iron, cobalt, manganese, chromium, platinum, and some other metals form, with the cyanides of the metals of the alkalies and the alkaline earths, compounds of a peculiar character in which the presence of the iron, or the cobalt, &c., cannot be detected by the usual tests for these metals. Some of these compounds are of considerable importance.

(1106) POTASSIC CYANIDE; KCN or $KCy=65{\cdot}1$.—This salt is formed when potassium is heated in cyanogen or hydrocyanic acid vapour, or when potassic hydrate is dissolved in a solution of hydrocyanic acid. It is most conveniently prepared by heating thoroughly dried potassic ferrocyanide to redness in an iron vessel, taking care to exclude the air, the reaction being $K_4FeC_6N_6=4KCN+FeC_2+N_2$. Most of the potassic cyanide may be poured off, in a fused state, from the iron carbide which settles at the bottom, and the remainder may be obtained by pulverizing the latter and extracting it with boiling alcohol, which deposits the cyanide in the crystalline state on cooling. It may also be obtained by heating to dull redness in a covered iron crucible a mixture of 8 parts of anhydrous potassic ferrocyanide, and 3 of dried potassic carbonate until the fused mass has lost its yellow colour, and ceases to give off bubbles of gas. The iron is separated in the form of a metallic powder, and subsides to the bottom of the crucible; the fused cyanide can then be poured off, as in the previous process, and solidifies on cooling to a milk-white mass. The cyanide thus obtained is, however, always mixed with a portion of cyanate, the reaction being shown in the following equation:

$$K_4FeC_6N_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2.$$

Potassic cyanide is prepared in considerable quantities for the purpose of dissolving the salts of gold and silver in the processes of electrotyping; it is also employed in photography.

If it be desired to avoid the presence of potassic cyanate, it may be got rid of by adding to the mixture of the carbonate and ferrocyanide, before fusion, one-eighth of its weight of charcoal, which at a red heat reduces the potassic cyanate to cyanide: the fused salt, when decanted from the iron, will then have a black aspect, owing to the presence of the charcoal which has been employed in excess. If it is to be used in solution immediately, it may be dissolved in water and filtered, or it may be purified by crystallization from boiling alcohol. When pure potassic cyanide is required, however, it is best to pass the vapour of dry hydrocyanic acid into a solution of potassic hydrate in absolute alcohol. It is then at once precipitated in the crystalline state.

Potassic cyanide forms colourless, deliquescent cubes; it has an alkaline reaction, and when moist emits an odour of hydrocyanic acid; it is highly poisonous. Its aqueous solution slowly decomposes at the ordinary temperature, and much more rapidly when boiled, giving rise to potassic formate and ammonia: $CNK + 2OH_2 = HCOOK + NH_3$. Fused potassic cyanide rapidly absorbs oxygen, so that it is a powerful and valuable reducing agent. The oxides of a large number of metals, including those of lead, copper, and iron, when thrown into the melted salt are immediately reduced to the metallic state, while potassic cyanate is formed. It may also be used in the laboratory as a reducing agent instead of black flux, in testing for arsenicum (841). Solutions of potassic cyanide dissolve metallic iron, zinc, nickel, and copper, with evolution of hydrogen, while potassic hydrate is produced. Silver and gold are also dissolved by the solution of potassic cyanide, if air be allowed free access, and double cyanides of potassium with those metals are formed. Cupric sulphide is soluble in an excess of potassic cyanide, and may be thus easily separated from cadmic sulphide, which is insoluble in this reagent.

(1107) Double Cyanides.—Potassic cyanide frequently produces a precipitate of a metallic cyanide when mixed with solutions of the metals, and in a great number of instances they are soluble in an excess of the potassic cyanide, forming crystallizable double salts. The cyanides of the metals of the other alkalies and of the alkaline earths, when substituted for potassic cyanide, produce similar double cyanides. The double cyanides which are formed in these cases are of two kinds or classes; those of the first class are highly poisonous, and comparatively unstable, being decomposed by dilute acids, such as hydrochloric acid. In such cases the potassic cyanide is decomposed, hydrocyanic acid is liberated, and the insoluble metallic cyanide is precipitated: the double salts which the cyanides of zinc, nickel, copper, and silver form with potassic cyanide belong to this class. When, for example, potassic nickelous cyanide is decomposed by hydrochloric acid nickelous cyanide is precipitated; the following reaction taking place:

$$NiCy_2, 2KCy + 2HCl = NiCy_2 + 2KCl + 2HCy.$$

The alkalies do not occasion precipitates in the solutions of the double cyanides. When these double cyanides are mixed with a solution of a metallic salt which, like plumbic acetate or cupric sulphate, is capable of furnishing an insoluble cyanide, a double insoluble cyanide is formed; for example:

$$NiCy_2, 2KCy + Pb(C_2H_3O_2)_2 = NiCy_2, PbCy_2 + 2KC_2H_3O_2.$$

The double cyanides of the second class are much more stable: the addition of dilute acids does not produce any precipitate of an insoluble cyanide, neither does it cause the liberation of hydrocyanic acid; the poisonous characters of the cyanides is also frequently absent in salts of this class. The double salts which the cyanides of cobalt, of iron, of chromium, and of platinum, form with potassic cyanide, are of this kind, and they may conveniently be regarded as compounds of potassium with hypothetical radicles, to which the terms cobalticyanogen, ferrocyanogen, ferricyanogen, chromicyanogen, and platinocyanogen, have been applied, since, from these salts, acids may be obtained which contain a certain number of atoms of hydrogen capable of being replaced by metals. For instance, the cyanide of potassium and iron, termed potassic ferrocyanide, which is represented by the formula, K_4FeCy_6, yields, when decomposed by hydrochloric acid, a compound termed hydroferrocyanic acid, H_4FeCy_6, containing 4 atoms of hydrogen instead of the 4 of potassium in the original salt :

$$\underset{\text{Potassic ferrocyanide.}}{K_4FeCy_6} + 4HCl = \underset{\text{Hydroferrocyanic acid.}}{H_4FeCy_6} + 4KCl.$$

The compound H_4FeCy_6 readily decomposes the metallic carbonates with effervescence.

(1108) DOUBLE CYANIDES.—The following are some of the principal insoluble metallic cyanides which yield double cyanides of the first class, *i.e.*, double salts which are decomposed and yield a precipitate on the addition of a dilute acid.

Zincic cyanide is white, and insoluble in water; with potassic cyanide it forms a soluble salt, $ZnCy,2KCy$, which may be obtained in large, regular, anhydrous, colourless octahedra. *Sodic zincic cyanide*, $2ZnCy_2,2NaCy,5OH_2$, may be obtained in brilliant plates, if sodic cyanide be substituted for potassic cyanide. Corresponding compounds containing cadmium and indium in place of zinc also exist. The *indic cyanide* is, however, easily decomposed when boiled with water, indic hydrate being formed, and hydrocyanic acid evolved. *Nickelous cyanide*, $NiCy_2$, forms an apple-green precipitate, which is very soluble in potassic cyanide, forming a double salt, $NiCy_2,2KCy,OH_2$, which crystallizes in oblique rhombic prisms of a yellow colour. *Cuprous cyanide*, Cu_2Cy_2, is a white insoluble powder obtained by treating an acid solution of cuprous chloride with potassic cyanide; it is soluble in ammonia and in dilute acids. Cupric sulphate yields with potassic cyanide a brownish-yellow precipitate, $CuCy_2$, which may be obtained in the pure state by treating recently precipitated cupric hydrate with hydrocyanic acid; it soon begins to give off cyanogen, becoming converted into a double cuproso-cupric cyanide, $Cu_2Cy_2,CuCy_2,5OH_2$. On boiling this with water it undergoes decomposition, cyanogen being evolved, and cuprous cyanide formed. The cuproso-cupric cyanide may also be obtained in bright green crystals by adding hydrocyanic acid to a solution of cupric sulphate. Cupric cyanide, $CuCy_2$, is soluble in excess of potassic cyanide, with evolution of cyanogen, and formation of cuprous cyanide; cuprous cyanide forms two crystallized double salts, $Cu_2Cy_2,2KCy$, and $Cu_2Cy_2,6KCy$. The latter is the more soluble salt of the two. On precipitating a solution of the former with plumbic acetate, suspending the plumbic cuprous cyanide thus obtained in water and decomposing it by sulphuretted hydrogen, a solution of *cuprocyanic acid*, $H_2Cu_2Cy_4$, is left. *Plumbic cyanide*, $PbCy_2$, is a white precipitate insoluble in water, or in a solution of potassic cyanide. Dilute sulphuric acid decomposes it with liberation of hydrocyanic acid.

(1109) ARGENTIC CYANIDE, or *Cyanide of Silver*; AgCN or $AgCy = 134$; *Sp. gr.* 3·943; is precipitated in dense white flocculi when hydrocyanic acid or potassic cyanide is added to a solution of argentic nitrate. It is nearly insoluble in *dilute* nitric acid even at a boiling temperature, but it is soluble in ammonia, and is decomposed by strong boiling nitric acid and by hydrochloric acid. When heated strongly it melts, and gives off cyanogen, leaving a residue of a grey colour, which appears to be a mixture of metallic silver and paracyanogen, or perhaps argentic para-cyanide. Argentic cyanide is freely soluble in solutions of the cyanides of potassium, sodium, barium, strontium, and calcium. These solutions give no precipitate with solutions of the metallic chlorides; indeed, argentic cyanide is dissolved by boiling solutions of the chlorides of the alkali and alkaline earthy metals. It is also soluble in a solution of argentic nitrate, as well as in solutions of potassic ferrocyanide and ferricyanide. When potassic ferrocyanide is used as the solvent, a dirty blue precipitate is formed, and the liquid becomes strongly alkaline. *Potassic argentic cyanide*, $AgCy,KCy = 199 \cdot 1$, is usually obtained in anhydrous octahedra or six-sided plates, but occasionally it forms rhombic prisms, $2AgCy,KCy,OH_2$. This salt is freely soluble in water and in boiling alcohol. It is extensively employed for electro-silvering, since its solution, if mixed with an excess of potassic cyanide and then submitted to electrolysis, deposits silver in compact coherent plates (295).

(1110) MERCURIC CYANIDE, or *Cyanide of Mercury*; $Hg(CN)_2$ or $HgCy_2 = 252$; *Sp. gr.* 3·77.—No compound of mercury and cyanogen corresponding to the mercurous salts is known, the addition of potassic cyanide to a solution of a mercurous salt producing a precipitate of metallic mercury, whilst mercuric cyanide remains in solution:

$$Hg_2(NO_3)_2 + 2KCy = Hg + HgCy_2 + 2KNO_3.$$

Mercuric cyanide may be prepared either by dissolving mercuric oxide in dilute hydrocyanic acid, in which the oxide is soluble with great facility, or by boiling a mixture of 4 parts of finely-powdered Prussian blue and 3 of mercuric oxide, also finely levigated, with 30 parts of water, until the undissolved portion has acquired a full brown colour: the filtrate on evaporation yields mercuric cyanide. It may also be procured by boiling 2 parts of mercuric sulphate with 1 part of potassic ferrocyanide and 8 of water:

$$K_4FeCy_6 + 3HgSO_4 = 3HgCy_2 + 2K_2SO_4 + FeSO_4.$$

Mercuric cyanide crystallizes in anhydrous rectangular prisms, which are colourless and transparent. It has a nauseous, metallic taste, and is very poisonous. It requires about 8 parts of cold water for solution; it is less soluble in ordinary alcohol, and nearly insoluble in absolute alcohol. Mercuric cyanide is decomposed when heated; if perfectly dry it yields cyanogen gas, metallic mercury, and a residue of paracyanogen; if moist, carbonic anhydride, ammonia, and hydrocyanic acid are produced.

Mercuric cyanide dissolves mercuric oxide freely, and forms an *oxycyanide*, $HgO,HgCy_2,=O\left\{\begin{matrix}HgCy\\HgCy\end{matrix}\right.$, which crystallizes in needles; it is sparingly soluble in cold water, and the liquid has an alkaline reaction. Mercuric cyanide does not give any precipitate of mercuric oxide on the addition of an alkali. When heated with sulphuric or hydrochloric acid it is decomposed, and hydrocyanic acid is given off. It is also decomposed by sulphuretted hydrogen. Mercuric cyanide forms double salts with the alkaline cyanides, the potassic compound, $2KCy,HgCy_2$, crystallizing in colourless octahedra; it also enters into combination with a great number of chlorides, bromides, iodides, cyanides, nitrates, and various other salts, forming with them crystallizable double salts. It does not occasion precipitates when mixed with the solutions of salts of zinc, cobalt, nickel, manganese, and other metals which yield cyanides insoluble in water, with the exception of the salts of palladium; from which it would appear that mercury has, so to speak, a stronger attraction for cyanogen than any of the metals, excepting palladium.

(1111) CYANIDES OF GOLD.—*Aurous cyanide;* $AuCy=222{\cdot}6$, may be obtained by several methods; the simplest consists in adding a solution of potassic cyanide to a dilute solution of auric chloride, as long as a precipitate is produced. It is a lemon-yellow insoluble powder, composed of microscopic hexagonal plates. It is decomposed by heat into cyanogen and metallic gold; boiling nitric, sulphuric, and hydrochloric acids do not decompose it unless very concentrated, and aqua regia acts upon it very slowly. It is soluble in sodic thiosulphate, in ammonic hydric sulphide, and in a solution of potassic ferrocyanide; but its most important solvent is potassic cyanide, with which it forms a double salt, $AuCy,KCy$, crystallizing in colourless rhombic octahedra, or in pearly scales.

Potassic aurocyanide; $KAu'Cy_2$.—This salt may be obtained by dissolving either aurous cyanide, sulphide of gold, or auric oxide, in a solution of potassic cyanide. The double cyanide is likewise formed by dissolving finely-divided metallic gold in a solution of potassic cyanide with exposure to the air. Potassic aurocyanide is largely used for gilding by means of the galvanic battery (955). Copper and silver articles may also be gilt by it without the aid of the battery, by mere immersion; portions of copper or of silver being dissolved during the operation. Potassic aurocyanide combines readily with iodine, forming the compound, $KAu'''Cy_2I_2,2OH_2$, from which the corresponding compounds containing chlorine and bromine are obtained on treating it with chlorine or bromine (*Bloomstrand, Journ. pr. Chem.* [2] iii. 213).

Potassic auricyanide; $KAu'''Cy_4$.—On boiling neutral auric chloride with a concentrated solution of potassic cyanide, and allowing it to cool, large transparent colourless plates of the double salt, $KCy, AuCy_3,OH_2$, are deposited. With argentic nitrate its solution yields a precipitate of argentic aurocyanide, and on suspending this in water and decomposing it by hydrochloric acid, taking care not to employ excess of the latter, a solution of *hydroauricyanic acid* is obtained. This deposits large colourless crystals of *hydric auricyanide,* $2AuHCy_4,3OH_2$, when evaporated *in vacuo.*

(1112) CYANIDES OF IRON.—Little is known accurately of the simple cyanides of iron. When potassic cyanide is mixed with ferrous sulphate free from ferric salt, an orange-brown precipitate partially soluble in acids is formed, which, according to Staedeler (*Ann. Chem. Pharm.,* cli. 1), consists of *potassic ferrous cyanide,* KFe_2Cy_5. This precipitate is re-dissolved by an excess of potassic cyanide, and converted into potassic ferrocyanide. The white compound obtained by decomposing Prussian blue by means of a current of sulphuretted hydrogen appears not to be a simple cyanide of iron, as was originally supposed by Robiquet. *Ferric cyanide* has not been procured in a separate form. When a solution of ferric chloride is mixed with one of potassic cyanide, a precipitate of hydrated ferric oxide is obtained, hydrocyanic acid is liberated, and potassic chloride is formed; with excess of potassic cyanide, potassic ferrocyanide is also produced. *Prussian blue, Turnbull's blue,* and the substance which Gmelin terms *Prussian green,* are compound cyanides of iron.

(1113) FERROCYANIDES AND FERRICYANIDES.—The cyanides of iron, when in combination with other cyanides, give rise to two important classes of compounds, which are represented by *potassic ferrocyanide,* the so-called yellow prussiate of potash, $K_4FeCy_6,3OH_2$, and *potassic ferricyanide,* the so-called red prussiate of potash, K_3FeCy_6. Liebig supposed that these two classes of salts contain two separate radicles, *ferrocyanogen,* $FeCy_6$, or Cfy^{iv}, and *ferricyanogen,* $FeCy_6$, or $Cfdy'''$; the first of these radicles being assumed to be tetrad or tetrabasic, the second triad or tribasic.

(1114) POTASSIC FERROCYANIDE, or *Prussiate of Potash;* $K_4Fe(CN)_6,3OH_2$ $K_4FeCy_6,3OH_2=368'4$, or $K_4Cfy^{iv}+54$.—This important salt is met with in commerce nearly in a state of purity. It is formed when nitrogenized matters are heated to redness with potassic carbonate and iron, and also when a ferrous salt is mixed with a solution of potassic hydrate supersaturated with hydrocyanic acid. It is manufactured on a large scale by heating dried blood, horns, parings of hides, and other animal matters containing nitrogen, with an equal weight of crude potassic carbonate, and about one-third of their weight of iron filings, in a covered iron pot. The reactions by which the ferrocyanide is produced are complicated. When animal matters are heated with potassic carbonate, the latter is reduced and the potassium combines with carbon and nitrogen to form potassic cyanide. A variable quantity of the iron which is added is at the same time converted into sulphide, owing to the action of the dipotassic sulphide (produced by the reduction of the potassic sulphate in the crude carbonate employed) upon the metal. When the mass is lixiviated, the potassic cyanide contained in the mixture attacks the metallic iron, and potassic ferrocyanide and potassic hydrate are formed: $12KCy + 2Fe + 2OH_2 + O_2 = 2K_4FeCy_6 + 4KHO$; if the air have not free access hydrogen is also evolved: $6KCy + Fe + 2OH_2 = K_4FeCy_6 + H_2 + 2KHO$. At the same time the potassic cyanide acts on the sulphide in the following manner: $6KCy + FeS = K_4FeCy_6 + K_2S$, yielding potassic ferrocyanide and potassic sulphide. Ferrous oxide is also readily dissolved by a solution of potassic cyanide, whilst potassic ferrocyanide is formed as in the previous cases: $6KCy + FeO + OH_2 = K_4FeCy_6 + 2KHO$. A knowledge of these reactions explains the formation of the ferrocyanide during the lixiviation practised in the course of the manufacture.

Potassic ferrocyanide crystallizes from an aqueous solution in large truncated pyramids of a lemon-yellow colour, containing 3 molecules of water; the crystals are tough, and split into laminæ with facility. It is soluble in about four parts of cold and in two of boiling water, but is insoluble in alcohol; the addition of a solution of potassic hydrate to a concentrated aqueous solution causes the separation of a portion of the salt in the crystalline state. Potassic ferrocyanide has a saline bitterish taste, and is not poisonous. Heated to 100° (212° F.) it loses the whole of its water of crystallization, and crumbles to a yellowish-white powder; when heated to redness in closed vessels it fuses, and undergoes decomposition, nitrogen being evolved, whilst potassic cyanide and carbide of iron are formed (1106). When dried and heated with black oxide of manganese, potassic cyanate is produced.

The iron in the ferrocyanide does not perform the part of a basyl for when a solution of this salt is submitted to electrolysis the iron accompanies the cyanogen to the negative electrode. The iron cannot be thrown down from an aqueous solution of the salt by the addition of any alkaline solution; but if the alkaline liquid be boiled with mercuric oxide, the iron is separated in the form of hydrated ferric oxide.

When distilled with dilute sulphuric acid, potassic ferrocyanide yields hydrocyanic acid (1100), but when it is heated with ordinary concentrated sulphuric acid, carbonic oxide, and a mixture of potassic, ammonic, and ferrous sulphates are produced (375). In this case the hydrocyanic acid which probably is first produced, is converted by the water contained in the sulphuric acid into formic acid and ammonia, but by contact with the sulphuric acid the formic acid H_2CO_2 is at once resolved into carbonic oxide and water. Potassic ferrocyanide is manufactured in large quantities for use in dyeing and calico printing; it is used also in the preparation of Prussian blue, as well as in the processes of electro-plating and electro-gilding, and is the source from which the compounds of cyanogen are usually prepared.

(1115) *Other Ferrocyanides.*—An aqueous solution of potassic ferrocyanide produces characteristic precipitates with many of the metallic salts, so that it is extensively employed as a qualitative test. The precipitate generally consists of a double ferrocyanide of potassium and the metal by which the precipitate is occasioned. The insoluble ferrocyanides cannot be precipitated in alkaline solutions; the liquid should therefore in all cases be slightly acid. Many of the precipitates are white, such as those of zinc, cadmium, nickel, manganese, tin, lead, bismuth, antimony, silver, and mercury; with the exception of the compounds of cadmium and manganese, these are insoluble in dilute hydrochloric acid. The most characteristic precipitates occasioned by potassic ferrocyanide are the following:—with the salts of cobalt a yellowish-green; with ferrous salts a white, becoming blue; with ferric salts a deep blue; and with cupric salts a chocolate-brown; with salts of uranium it also gives a brown precipitate.

The following is a list of some of the ferrocyanides in which the whole or a part of the potassium of potassic ferrocyanide is displaced by another metal:

Potassic ferrocyanide	K_4FeCy_6.
Tripotassic sodic ferrocyanide	$K_3NaFeCy_6$.
Dipotassic disodic ferrocyanide	$K_2Na_2FeCy_6$.
Potassic trisodic ferrocyanide	KNa_3FeCy_6.
Sodic ferrocyanide	Na_4FeCy_6.
Dipotassic baric ferrocyanide	$K_2BaFeCy_6$.
Dibaric ferrocyanide	Ba_2FeCy_6.
Dipotassic cupric ferrocyanide	$K_2CuFeCy_6$.
Dipotassic tricupric ferrocyanide	$K_2Cu_3(FeCy_6)_2$.

(1116) HYDROFERROCYANIC ACID, H_4FeCy_6.—This compound was originally obtained by Porrett, who decomposed potassic ferrocyanide by means of tartaric acid. A better plan consists in preparing a concentrated aqueous solution of the ferrocyanide, boiling it to expel the air, and then allowing it to cool in a vessel provided with a good cork to exclude air. Ether is now added, and an excess of hydrochloric acid, which has also been deprived of air by boiling. On agitating the mixture, white scales of hydroferrocyanic acid are deposited;

$$K_4FeCy_6 + 4HCl = H_4FeCy_6 + 4KCl.$$

These crystals must be washed with a mixture of alcohol and ether, and dried *in vacuo* over sulphuric acid. Liebig adds by degrees to a cold saturated solution of potassic ferrocyanide an equal volume of hydrochloric acid; the white precipitate of hydroferrocyanic acid thus obtained should be washed with hydrochloric acid, dried *in vacuo* upon a tile, and caused to crystallize from its solution in alcohol by the addition of ether: if air be excluded it is then obtained in large colourless crystals.

When hydroferrocyanic acid is exposed to the air, it absorbs oxygen and becomes blue; its solution, when boiled, evolves hydrocyanic acid, and deposits a white insoluble matter containing both iron and cyanogen. By exposure to the air this white substance absorbs oxygen, becoming converted into the so-called basic Prussian blue.

(1117) **POTASSIC FERRICYANIDE**, or *Red prussiate of potash*; $K_6Fe_2Cy_{12}$ or $K_6(Cfdy)'''_2 = 658{\cdot}6$.—When a current of chlorine gas is passed through a dilute solution of potassic ferrocyanide the liquid quickly changes colour and becomes of a deep red, the reaction which occurs being the following:

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

If the current of the gas be arrested, as soon as the liquid ceases to give a blue precipitate with ferric salts, the solution on evaporation yields crystals of potassic ferricyanide. The ferricyanide may be obtained by a second crystallization in transparent, anhydrous, right rhombic prisms of a beautiful ruby-red colour; and if the operation be performed on a large scale these crystals often attain a large size: they are soluble in about 2·5 parts of cold water and in 1·3 parts of boiling water, but are insoluble in alcohol: unlike the ferrocyanide, it is very poisonous. If the action of the chlorine be too long continued, the red salt is in its turn partially decomposed, and a green compound is formed which interferes with the crystallization of the red salt. This *Prussian green*, as the compound is termed, according to the analysis of Pelouze, may be represented by the formula $FeCy_2,Fe_2Cy_6,4OH_2$, or it is the *magnetic cyanide* corresponding to the magnetic oxide of iron, FeO,Fe_2O_3; it is by no means certain, however, that it really has this composition. Potassic ferricyanide is prepared on the large scale for the use of the calico-printer, generally by decomposing the solid yellow salt by exposing it in powder to the action of a current of chlorine. It is also formed by the action of most oxidizing agents on potassic ferrocyanide, and when a solution of the latter salt is decomposed by the voltaic current in a diaphragm cell, potassic ferricyanide makes its appearance in the solution at the positive electrode.

It has been suggested that the iron in the ferrocyanides is in the ferrous state, whilst in the ferricyanides it is in the ferric state: according to this supposition, therefore, the action of chlorine on potassic ferrocyanide not only removes potassium, but at the same time changes the iron from the ferrous to the ferric state:

$$2K_4Fe''Cy_6 + Cl_2 = K_6(Fe_2)^{vi}Cy_{12} + 2KCl.$$

A solution of potassic ferricyanide when mixed with an excess of potassic hydrate furnishes a liquid possessed of considerable oxidizing power; thus, it converts the hydrated protoxides of manganese, lead, and tin into peroxides of these metals, whilst the ferricyanide passes into the condition of ferrocyanide of potassium:

$$K_6Fe_2Cy_{12} + Mn(OH)_2 + 2KHO = 2K_4FeCy_6 + MnO(OH)_2 + OH_2.$$

The same solution is employed by the calico-printer for the purpose of discharging the blue colour of indigo from calico (Mercer). The red prussiate burns with scintillation when introduced into the flame of a candle. Potassic ferricyanide produces insoluble compounds when mixed with solutions of many of the metallic salts, and as the colours of these precipitates are often characteristic, this salt is frequently employed in the laboratory as a qualitative test for metals in neutral or feebly acid solutions. It gives no precipitate with the ferric salts, but a splendid blue (Turnbull's blue) when mixed with those of the ferrous salts; with salts of zinc it yields an orange precipitate, with those of cadmium a yellow, with nickel a yellowish-green, with cobalt a dark reddish-brown, with copper a yellowish-green, with manganous salts a brown, with stannous salts a white, with silver salts an orange, and with mercurous salts a brownish-red. These precipitates, with the exception of those with zinc and tin, are insoluble in dilute hydrochloric acid. Plumbic ferricyanide separates in dark reddish-brown crystals on mixing concentrated solutions of plumbic nitrate and potassic ferricyanide.

The following table exhibits the composition of a few ferricyanides:

Potassic ferricyanide	$K_6Fe_2Cy_{12}$
Dipotassic tetrasodic ferricyanide* . .	$K\,Na_4Fe_2Cy_{12}$

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* Reindel obtained this salt on allowing a solution containing potassic ferricyanide and sodic nitrate to crystallize (*Journ. pr. Chem.*, cii. 43).

Sodic ferricyanide	$Na_6Fe_2Cy_{12}$
Dipotassic dibaric ferricyanide	$K_2Ba_2Fe_2Cy_{12}$

(1118) *Hydroferricyanic acid*, $H_6Fe_2Cy_{12}$.—This compound may be obtained by decomposing plumbic ferricyanide suspended in water with an equivalent quantity of dilute sulphuric acid. On filtering from the plumbic sulphate and evaporating, the acid forms reddish-brown deliquescent crystals. Schafarik, by mixing a cold saturated aqueous solution of potassic ferricyanide with two or three times its bulk of fuming hydrochloric acid, obtained brownish-green thin brilliant needles, which he believed to be hydroferricyanic acid; according to Reindel, however, they can never be obtained free from potassium.

(1119) PRUSSIAN BLUE.—The name *Prussian blue* is applied to a number of blue substances, some of which are largely employed in the arts as pigments: they are prepared either by precipitating a solution of potassic ferrocyanide with a ferric salt or a mixture of ferric and ferrous salts, by the addition of a ferrous salt to a solution of potassic ferricyanide, or by oxidizing ferrous dipotassic ferrocyanide.

Whenever a solution of potassic ferrocyanide is added to one of a soluble ferric salt a beautiful blue precipitate is produced, which always contains potassium even if a large excess of the ferric salt has been employed; if, however, a solution of hydroferrocyanic acid be mixed with an excess of a ferric salt, a blue precipitate is obtained free from potassium, which has the composition $Fe_7Cy_{18},18OH_2$ (Williamson).

(1120) FERROUS DIPOTASSIC FERROCYANIDE.—The addition of a solution of a ferrous salt to one of potassic ferrocyanide produces a white precipitate of ferrous dipotassic ferrocyanide if access of air be entirely prevented, otherwise it has a greenish tint; this appears to be identical with Everitt's white salt (p. 93) being formed by the displacement of half the potassium in the potassic ferrocyanide by the equivalent quantity of iron, thus: $K_4FeCy_6 + Fe''Cl_2 = K_2Fe''(FeCy_6) + 2KCl$. When treated with a solution of potassic hydrate it is re-converted into potassic ferrocyanide with separation of ferrous hydrate, which rapidly undergoes oxidation: $K_2Fe''(FeCy_6) + 2KOH = K_4FeCy_6 + Fe(OH)_2$. When potassic ferrous ferrocyanide is exposed to the air, it becomes oxidized, and turns blue, forming a compound termed *Basic Prussian blue;* a strong acid removes ferric oxide from this basic Prussian blue, leaving, it is said, Prussian blue.

(1121) DIFERROUS DIPOTASSIC FERRICYANIDE.—On mixing solutions containing one molecule of ferric chloride and two molecules of potassic ferrocyanide, and then adding alcohol, a magnificent violet-blue precipitate is obtained. This, the so-called *soluble Prussian blue,* although insoluble in saline solutions, is readily soluble in pure water. After being dried at 110° (230° F.), however, it becomes insoluble. *Diferrous dipotassic ferricyanide,* or soluble Prussian blue, has the composition $K_2Fe_2''(Fe_2Cy_{12}),8OH_2$, (Reindel, *Journ. pr. Chem.*, cii. 38, 255), and is formed in the following manner:

$$2K_4Fe''Cy_6 + (Fe_2)^{vi}Cl_6 = K_2Fe_2''(Fe_2)^{vi}Cy_{12} + 4KCl.$$

The ferrocyanide having been converted into a ferricyanide by the oxidizing action of the ferric chloride.

Williamson finds that Everitt's white salt *ferrous dipotassic ferrocyanide,* $K_2Fe''(FeCy_6)$, when treated with oxidizing agents is decomposed, and a blue salt is formed, which is identical with the diferrous dipotassic ferricyanide above mentioned. This is best effected by boiling the white precipitate with nitric acid, diluted with twenty parts of water; as the liquid approaches the boiling point a copious evolution of nitric oxide occurs, two molecules of the white salt lose two atoms of potassium, and *ferrous dipotassic ferricyanide* is formed. Care is required to prevent the action of the acid from proceeding too far, otherwise Pelouze's Prussian green is apt to be formed. Diferrous dipotassic ferricyanide, when treated with a solution of potassic ferrocyanide, is reconverted into ferrous dipotassic ferrocyanide, and pure potassic ferricyanide is obtained in solution, provided the blue ferricyanide has been employed in slight excess:

$$K_2Fe''_2(Fe_2)^{vi}Cy_{12} + 2K_4FeCy_6 = K_6(Fe_2)^{vi}Cy_{12} + 2K_2Fe''FeCy_6.$$

The pale blue residue on the filter, which consists of ferrous dipotassic ferrocyanide mixed with the excess of the blue salt, may be again converted into the latter by treatment with nitric acid, and in this way be used repeatedly for converting potassic ferrocyanide into ferricyanide. Similarly, when potassic ferrocyanide is added to a solution of the soluble Prussian blue, the white potassic ferrous ferrocyanide is precipitated, whilst potassic ferricyanide remains in solution.

According to Reindel, the addition of ferric chloride does not cause a precipitate in a solution of the soluble Prussian blue; it must be observed, however, that when it is decomposed by an alkaline hydrate or carbonate, it yields potassic ferrocyanide and ferric hydrate. This is explained by supposing that, in the first instance, ferrous hydrate and potassic ferricyanide are formed, thus:

$$K_2Fe''_2(Fe_2)^{vi}Cy_{12}+4KHO=K_6(Fe_2)^{vi}Cy_{12}+2Fe''(OH)_2,$$

and that the ferrous hydrate in the presence of an alkali then reduces the ferricyanide to ferrocyanide:

$$K_6(Fe_2)^{vi}Cy_{12}+2Fe''(OH)_2+2KHO=2K_4Fe''Cy_6+(Fe_2)^{vi}(OH)_6.$$

(1122) TRIFERROUS FERRICYANIDE.—The precipitate of triferrous ferricyanide, $Fe_3''(Fe_2)^{vi}Cy_{12}$, obtained on adding a ferrous salt to a solution of potassic ferricyanide, constitutes a highly valued and brilliant variety of Prussian blue, commercially known as *Turnbull's blue*. This precipitate, however, unless digested for some time with an excess of a ferrous salt, always retains potassium, probably present as diferrous dipotassic ferricyanide, $K_2Fe_2''(Fe_2)^{vi}Cy_{12}$. Triferrous ferricyanide is also obtained by precipitating a solution of the "soluble Prussian blue" with a ferrous salt (Reindel, *loc. cit.*):

$$K_2Fe_2''(Fe_2)^{vi}Cy_{12}+Fe''Cl_2=Fe_3''(Fe_2)^{vi}Cy_{12}+2KCl.$$

Turnbull's blue may be distinguished from the other Prussian blues by the action of a solution of potassic hydrate, which decomposes it, yielding potassic ferrocyanide and hydrated magnetic oxide of iron or ferroso-ferric oxide, whilst the other blues when similarly treated give potassic ferrocyanide and ferric oxide; the formation of the hydrated ferroso-ferric oxide may be explained by the following equations:

$$Fe_3''(Fe_2)^{vi}Cy_{12} + 6KHO = K_6(Fe_2)^{vi}Cy_{12} + 3Fe''(OH)_2;$$
$$K_6(Fe_2)^{vi}Cy_{12} + 2Fe(OH)_2 + 2KHO = 2K_4Fe''Cy_6 + Fe_2(OH)_6;$$
$$Fe(OH)_2 + Fe_2(OH)_6 = OH_2 + Fe_3O(OH)_6 \text{ or } Fe_3O_4,3OH_2.$$

Commercial Prussian blue.—When large quantities of Prussian blue are required, Liebig recommends that 11 parts of crystallized ferrous sulphate be dissolved in water, and divided into two equal portions; one part is then to be mixed with 2 parts of hydrochloric acid, and chloride of lime gradually added until the whole of the ferrous salt is converted into a ferric salt; it is then to be mixed with the other portion of the solution, and a solution of 10 parts of potassic ferrocyanide is to be added. Prussian blue, however, is also manufactured on the large scale by oxidizing the precipitate of ferrous dipotassic ferrocyanide produced by adding ferrous sulphate to a solution of potassic ferrocyanide. Commercial Prussian blue is generally contaminated with alumina, and sometimes with chalk, plaster of Paris, and starch; it is met with in cubical or irregular masses of a dark blue colour, which when pressed with a hard body, acquire a coppery lustre resembling that of indigo.

From the manner in which it is prepared it is evident that it must be a mixture, containing variable proportions of the violet-blue compound, diferrous dipotassic ferricyanide, $K_2Fe''_2(Fe_2Cy_{12})$, and of Turnbull's blue or triferrous ferricyanide, $Fe''_3(Fe_2Cy_{12})$. It is a noteworthy fact, moreover, that there is a certain relation between the tint of the blue prepared by the ordinary methods and the amount of potassium in it. This can be easily understood when it is remembered that the potassium is present as diferrous dipotassic ferricyanide, which has a violet-blue colour, whilst the triferrous ferricyanide is a pure bright blue; so that the tint of the product inclines more or less to violet according to the relative proportions of the two compounds contained in the mixture.

Prussian blue is insoluble in water and in weak acids, and has neither taste nor smell. After it has been washed with dilute hydrochloric acid, it may, however, be rendered soluble by triturating it with one-sixth of its weight of crystallized oxalic acid. When this solution is diluted with forty or fifty parts of water, it forms a blue liquid, which is used as a writing ink. Prussian blue is also soluble in a cold solution of ammonium tartrate, forming a violet-coloured liquid. Concentrated sulphuric acid produces a white pasty mass when triturated with Prussian blue, but on the addition of water sulphuric acid is separated, and the blue pigment is reproduced. Prussian blue is decomposed when heated with concentrated sulphuric, nitric, or hydrochloric acid; it is also decomposed by the action of chlorine. When boiled with mercuric oxide, mercuric cyanide is produced and ferric oxide is separated.

Prussian blue contains water, which cannot be expelled by heat without decomposing the compound. If heated in the open air it becomes kindled on the approach of an ignited body, and burns like tinder, leaving a residue of ferric oxide.

(1123) **Nitroprussides.**—The nitroprussides were originally procured by the following process, recommended by Playfair, by whom these salts were discovered (*Phil. Trans.*, 1849, p. 481):

Common nitric acid is to be diluted with an equal bulk of water, and when cold, powdered potassic ferrocyanide is to be added in the proportion of 2 molecules or 422 parts of the ferrocyanide to 5 molecules or 315 parts of the acid, HNO_3. The mixture gradually assumes a brown colour, cyanogen and hydrocyanic acid are liberated, whilst a brisk effervescence occurs, owing to the escape of carbonic anhydride and nitrogen, and the salt is dissolved, forming a mixture of potassic ferricyanide, nitroprusside, and nitrate: the solution should now be heated by means of a water-bath, until gas ceases to be evolved, and the liquid, instead of giving a blue precipitate with a ferrous salt, produces a dark green or slate-coloured precipitate. It must then be allowed to cool, by which means a large quantity of potassic nitrate, mixed with a small proportion of oxamide, will be separated. The strongly-coloured mother-liquor should next be neutralized with potassic or sodic carbonate, which causes a greenish-brown precipitate, and the liquid, after filtration, evaporated and allowed to crystallize. Sodic nitroprusside crystallizes more readily than the potassic salt which, although anhydrous, is somewhat deliquescent.

Hadow (*Journ. Chem. Soc.*, 1866, 341) greatly improved this process by mixing a solution of potassic ferricyanide with one of mercuric chloride, acidulating with acetic acid, and then adding a definite quantity of sodic nitrite. According to Staedeler, however (*Zeits. Chem.*, 1869, 559), the presence of mercuric chloride is not necessary, for he finds that the nitroprusside is produced even more readily when a solution of potassic ferricyanide and potassic nitrite is acidulated with a dilute mineral acid, the reaction being:

$$\underset{\text{Potassic ferricyanide.}}{K_6Fe_2Cy_{12}} + 2KNO_2 + 4HCl = \underset{\text{Potassic nitroprusside.}}{K_4Fe_2(NO)_2Cy_{10}} + 4KCl + 2OH_2 + Cy_2.$$

(1124) *Composition of the Nitroprussides.*—Hadow assigned to these compounds the formula $M_4Fe_2N_3O_3Cy_{10}$, as he found that nitrous anhydride, N_2O_3, converted hydroferricyanic acid into hydronitroprussic acid, whilst nitric oxide did not; the more recent researches of Staedeler, however, tend to prove that their formula is that proposed by Gerhardt, or rather double that formula—namely, $M_4Fe_2(NO)_2Cy_{10}$.

(1125) *Hydronitroprussic acid;* $H_4Fe_2(NO)_2Cy_{10}$.—This acid is formed when the vapour of nitrous anhydride is passed into an aqueous solution of hydroferricyanic acid, cyanogen being evolved:

$$H_6Fe_2Cy_{12} + 2NO.OH = H_4Fe_2(NO)_2Cy_{10} + Cy_2 + 2OH_2.$$

An aqueous solution of the acid may be prepared by decomposing argentic nitroprusside with dilute hydrochloric acid. The solution yields dark red deliquescent crystals of the formula, $H_4Fe_2(NO)_2Cy_{10}, 2OH_2$, by evaporation *in vacuo.*

(1126) *Sodic Nitroprusside;* $Na_4Fe_2(NO)_2Cy_{10}, 4OH_2$.—This salt crystallizes in fine prisms of a ruby-red colour, which require about 2·5 parts of cold water for solution. Its solution is decomposed by exposure to the sun's rays, Prussian blue being deposited, while nitric oxide escapes. *Baric nitroprusside,* $Ba_2Fe_2(NO)_2Cy_{10}, 6OH_2$, crystallizes in fine octahedra of a dark red colour.

The nitroprussides give a pale green precipitate with salts of copper, and a flesh-coloured precipitate with those of silver. With salts of zinc a salmon-coloured precipitate is produced; with salts of nickel, a dirty white; with salts of cobalt, a flesh-coloured precipitate; and with ferrous salts, a salmon-coloured precipitate is formed. The ferric salts, and the salts of lead, of mercury, and of tin, give no precipitates with the nitroprussides. Chlorine is without effect upon solutions of the nitroprussides; but they are decomposed when boiled with the alkalies, part of the iron being separated as a crystalline hydrated ferric oxide, while the solution becomes orange-coloured, and is found to contain a nitrite and a ferrocyanide. They are also decomposed by boiling sulphuric acid. If their solutions be boiled with mercuric oxide, nitric oxide is evolved, and mercuric cyanide is formed. Sulphuretted hydrogen also decomposes them. The most delicate and characteristic test for the nitroprussides is the production of a magnificent purple colour when mixed with solutions of the alkaline monosulphides, such as K_2S or KHS. This coloration is very intense, and may be employed to indicate very minute traces either of a soluble sulphide or of a nitroprusside. The colour, however, speedily disappears if any of the polysulphides are present. It appears to be due to the formation of a double salt of the nitroprusside with the sulphide of the alkali-metal. By boiling the liquid, nitrosulphide of iron and of the alkali-metal is obtained.

(1127) COBALTOCYANIDES AND COBALTICYANIDES.—When potassic cyanide is added to a salt of cobalt, it gives a reddish-brown precipitate, $CoCy_2$, which is soluble in an excess of the precipitant. The double cyanide of cobalt and potassium, *potassic cobaltocyanide,* $4KCy,CoCy_2$ or K_4CoCy_6, thus formed may be precipitated in the crystalline state by adding alcohol to the solution. It is decomposed on the addition of hydrochloric acid, cobaltous cyanide being precipitated; but if it be heated or exposed to the air *potassic cobalticyanide* is produced, which corresponds in composition to potassic ferricyanide.

POTASSIC COBALTICYANIDE; $K_6Co_2Cy_{12}$.—This salt, which was discovered by Gmelin, crystallizes in yellowish anhydrous flattened prisms, isomorphous with those of potassic ferricyanide; it is sparingly soluble in water. It may be obtained either by dissolving cobaltous cyanide in an excess of potassic cyanide, and exposing it to the air, or by dissolving hydrated cobaltous oxide by the aid of a gentle heat in a solution of potassic hydrate, supersaturated with hydrocyanic acid; in both cases oxygen is absorbed:

$$4CoCy_2 + 12KCy + 4HCy + O_2 = 2K_6Co_2Cy_{12} + 2OH_2.$$

If the solutions be boiled in closed vessels the same compound is formed, but hydrogen is evolved:

$$2CoCy_2 + 8KCy + OH_2 = K_6Co_2Cy_{12} + 2KOH + H_2.$$

The corresponding salt of *sodium*, $Na_6Co_2Cy_{12}, 4OH_2$, crystallizes in long, transparent, colourless needles; that of *barium*, $Ba_3Co_2Cy_{12}, 20OH_2$, in efflorescent prisms. The latter may be obtained by treating a mixture of cobaltous sulphate and baric carbonate with hydrocyanic acid. Other soluble cobalticyanides may be conveniently prepared from the baric salt by double decomposition with the respective sulphates. Solutions of cobalticyanides occasion precipitates with a large number of metallic salts. Cobalticyanide of zinc is white; that of nickel is gelatinous, and of a pale blue; that of cobalt is of a pale red; that of copper of a pale blue; the ferrous, manganous, and stannous, as well as mercurous and argentic cobalticyanides, are white; salts of lead give no precipitate with the soluble cobalticyanides.

HYDROCOBALTICYANIC ACID; $H_6Co_2Cy_{12}, 2OH_2$, crystallizes in colourless needles from its aqueous solution, which may be obtained by decomposing cupric cobalticyanide suspended in water, by sulphuretted hydrogen. It may also be prepared by adding sulphuric acid and then alcohol to a concentrated solution of potassic cobalticyanide, filtering from the precipitated potassic sulphate, and evaporating.

(1128) MANGANOCYANIDES AND MANGANICYANIDES.—*Potassic manganocyanide*, $K_4MnCy_6, 3OH_2$, isomorphous with the corresponding iron compound, is prepared by digesting manganous carbonate with a concentrated solution of potassic cyanide, or by adding potassic cyanide to a solution of manganous acetate, until the green precipitate, $KCy,MnCy_2$, at first formed, is re-dissolved, and then precipitating the manganocyanide with alcohol. It crystallizes in square plates of a deep violet colour, which dissolve readily in water, forming a colourless solution; after a time, however, this decomposes, depositing the green compound, $KCy,MnCy_2$. *Sodic manganocyanide* crystallizes in transparent octahedra of an amethyst colour. *Potassic manganicyanide*, $K_6Mn_2Cy_{12}$, crystallizes in reddish-brown prisms, isomorphous with the ferricyanide, and is produced when a solution of the manganocyanide is heated or exposed to the air.

(1129) CHROMICYANIDES.—Chromic salts yield with potassic cyanide a pale bluish-grey precipitate, Cr_2Cy_6, which is not soluble in excess of the potassic cyanide; but if a mixture of hydrated chromic oxide with a solution of potassic hydrate and an excess of hydrocyanic acid, be exposed to the air, the liquid acquires a reddish-brown colour, and a potassic chromicyanide is formed (Beckmann), corresponding to the ferricyanides and cobalticyanides. These salts are of small importance, and have been but little examined. *Potassic chromicyanide*, $K_6Cr_2Cy_{12}$, forms brownish-red anhydrous prisms; its solution precipitates argentic nitrate, white; salts of cobalt, blue; and ferrous salts of a brick-red; but it gives no precipitate with ferric salts, or with plumbic nitrate.

(1130) OSMIOCYANIDES AND RUTHENIOCYANIDES.—These compounds correspond in composition with the ferrocyanides, and the potassic salts of all three are isomorphous. The precipitates they form when mixed with salts of copper, iron, zinc, and lead, closely resemble those obtained with the ferrocyanides. *Potassic osmiocyanide*, K_4OsCy_6, $3OH_2$, is easily prepared by treating potassic osmate with potassic cyanide, evaporating to dryness, and gently igniting. On dissolving the calcined mass in a small quantity of hot water a solution is obtained which deposits the salt in large crystals on cooling. *Hydroosmiocyanic acid*, H_4OsCy_6, is obtained in the crystalline state on adding hydrochloric acid to a concentrated solution of the potassic salt.

(1131) PLATINOCYANIDES.—Gmelin ascertained that platinum is capable of entering into combination with cyanogen, and forming a series of double cyanides, which are amongst the most beautiful crystalline substances known; these compounds, however, are not analogous in composition to the foregoing, as may be seen from an inspection of the following formulæ:

Hydroplatinocyanic acid . . . . . H_2PtCy_4.
Potassic platinocyanide . . . . . K_2PtCy_4, $3OH_2$.

Potassic platinocyanide is best formed by dissolving platinous chloride in a solution of potassic cyanide, and evaporating the liquid until the salt crystallizes out on cooling:

$$PtCl_2 + 4KCy = K_2PtCy_4 + 2KCl.$$

It may also be obtained by fusing potassic ferrocyanide with spongy platinum, or by heating a concentrated solution of platinic chloride with an excess of potassic cyanide:

$$PtCl_4 + 6KCy = K_2PtCy_4 + 4KCl + C_2N_2.$$

This beautiful salt forms long transparent rhombic prisms, containing $3OH_2$, which are yellow by transmitted, and blue by reflected light; it is very soluble in water, but more sparingly so in alcohol and in ether. *Magnesic platinocyanide*, $MgPtCy_4,7OH_2$, is a beautiful salt which crystallizes in rosettes from its solution in a mixture of alcohol and ether: these crystals form square prisms, which are of a rich crimson by transmitted light, and green or blue by reflected light; they are very soluble in water, and the solution is colourless.

The changes of colour which this salt experiences by change in its condition of hydration are very remarkable. The ordinary red salt with $7OH_2$ when gently warmed, even under water, becomes yellow, and if crystallized at 71° (160° F.) yellow crystals with $6OH_2$ are deposited. At 100° (212° F.) the salt still retains $2OH_2$ when it is white, and between 150° and 200° (300° and 400° F.) it becomes anhydrous, and is then yellow. These singular changes of colour may be strikingly displayed by allowing a strong solution of the salt to evaporate on a sheet of white paper. When dry a crimson surface is obtained, but a drop of water upon any point destroys the colour at that spot instantly;

on drying it again reappears. When heated, the red salt first becomes yellow; as the temperature rises it is rendered white; and by a somewhat stronger heat it again becomes yellow. By breathing on the paper, the salt resumes the water that it had lost, the yellow spot becoming successively white, yellow, and eventually crimson (Hadow).

HYDROPLATINOCYANIC ACID, H_2PtCy_4, crystallizes from its aqueous solution with $5OH_2$ in deep red prisms having a bluish black fluorescence. It may be obtained by decomposing the mercurous, cupric, or argentic salt suspended in water by sulphuretted hydrogen, and evaporating the solution.

The most characteristic tests of the platinocyanides are the formation of a beautiful smalt-blue precipitate when a platinocyanide is added to a solution of mercurous nitrate in excess, and a flocculent blue precipitate with cupric salts: with argentic nitrate it yields a white precipitate. The platinocyanides are remarkable for their strong tendency to form double salts; amongst others a very beautiful double salt of potassium and magnesium, $MgPtCy_4,K_2PtCy_4,7OH_2$, may be obtained.

(1132) PLATINICYANIDES.—There is another very beautiful series of salts, commonly termed the platinicyanides, which are produced by the action of oxidizing agents, such as chlorine, bromine, nitric acid, &c., on the platinocyanides; they crystallize in prisms of a coppery lustre when viewed by reflected light, but they appear to be green by transmitted light, and polarize light powerfully; their solutions, however, are colourless. These salts, when dissolved in water, produce a white precipitate with argentic and mercuric salts, a blue with the mercurous salts, and a greenish-blue with the cupric salts. The platinicyanides have been carefully examined by Hadow, who has shown that the usually received formula, M_2PtCy_5, is erroneous, and that they are more complicated in structure. The salt formerly known as potassic platinicyanide is really a double salt of potassic platinocyanide and platinichlorocyanide:

$$K_{12}Pt_6Cy_{24}Cl_2,\ 21OH_2\ =\ 5K_2PtCy_4,\ K_2PtCy_4Cl_2,\ 21OH_2.$$

Salts exist, moreover, which correspond in appearance with this, containing in place of the two atoms of chlorine, either Br_2, or NO_2, or SO_4. In order to prepare these compounds in a state of purity, Hadow (*J. Chem. Soc.*, xiii. 106) mixes the platinocyanide with the platinichlorocyanide, or one of the corresponding compounds, in the ratio of 5 molecules of the former with 1 molecule of the latter; if the solution be of a proper degree of concentration the pure salt separates after a time.

Potassic platinocyanide unites with iodine, forming *potassic platini-iodocyanide*, $K_2PtCy_4I_2$, from which, by treatment with chlorine or bromine, the corresponding bromo- and chloro-platinicyanide are readily obtained in a state of purity. The corresponding hydrogen compounds are produced by decomposing the baric salts with dilute sulphuric acid. *Hydric platinibromocyanide*, or hydroplatinibromocyanic acid, thus prepared, crystallizes in long yellow needles; it is a strong acid, which readily dissolves metallic zinc, and forms zincic platinibromocyanide (Biomstrand, *Journ. pr. Chem.* [2], iii. 207).

(1133) PALLADIOCYANIDES.—When a solution of a salt of palladium is mixed with one of mercuric cyanide, a yellowish-white precipitate of palladious cyanide is formed; this precipitate is not decomposed by acids, but may be dissolved by means of potassic cyanide, with which it forms a double salt, crystallizing in colourless rhomboidal prisms, $K_2PdCy_4, 3OH_2$. The palladiocyanides are isomorphous with the corresponding platinocyanides.

(1134) RHODICYANIDES and IRIDICYANIDES.—Both rhodium and iridium yield double cyanides analogous to the ferricyanides, but potassic rhodicyanide is decomposed by acetic acid, with separation of the insoluble rhodic cyanide. This reaction may be employed in the separation of rhodium from iridium, since acetic acid does not decompose the iridium salt.

Potassic iridicyanide, $K_6Ir_2Cy_{12}$ (Claus), forms four-sided colourless crystals, and is characterized by giving a deep indigo-blue precipitate with the cupric salts, and a bright yellow with the ferric salts.

It appears from the foregoing statements, that cyanogen has a strong tendency to produce, with several of the metals, electronegative compounds, which form with hydrogen a series of well-marked acids: the number of atoms of metal which are thus united with the cyanogen to constitute the radicles of these acids, varying with the nature of the metal. These acids may be divided into classes, according to the number of hydrogen atoms displaceable by metals which they contain. The composition of the potassium salts of the different classes is exhibited in the following table:

Acid: monobasic	Auricyanide . . .	$KAu'''Cy_4$.
	Aurichlorocyanide .	$KAu'''Cy_2Cl_2$.
Acid: dibasic	Platinocyanide . .	$K_2Pt''Cy_4, 3OH_2$.
	Platinichlorocyanide .	$K_2Pt^{iv}Cy_4Cl_2, 2OH_2$.
	Palladiocyanide . .	$K_2Pd''Cy_4, 3OH_2$.
Acid: tetrabasic	Ferrocyanide . . .	$K_4Fe''Cy_6, 3OH_2$.
	Manganocyanide . .	$K_4Mn''Cy_6, 3OH_2$.
	Osmiocyanide . . .	$K_4Os''Cy_6, 3OH_2$.
	Rutheniocyanide . .	$K_4Ru''Cy_6, 3OH_2$.
Acid: hexabasic	Ferricyanide . . .	$K_6(Fe_2)^{vi}Cy_{12}$.
	Cobalticyanide . .	$K_6(Co_2)^{vi}Cy_{12}$.
	Manganicyanide . .	$K_6(Mn_2)^{vi}Cy_{12}$.
	Chromicyanide . .	$K_6(Cr_2)^{vi}Cy_{12}$.
	Iridicyanide . . .	$K_6(Ir_2)^{vi}Cy_{12}$.
	Rhodicyanide . . .	$K_6(Ro_2)^{vi}Cy_{12}$.

(1135) CHLORIDES OF CYANOGEN.—Chlorine forms with cyanogen two polymeric compounds, both of which are extremely poisonous: one is liquid, the other is solid.

CYANIC CHLORIDE or *Liquid Chloride of Cyanogen*, $CNCl$ or $CyCl = 61\cdot5$.—This compound is prepared by passing a rapid current of chlorine through a mixture of 1 part of anhydrous hydrocyanic acid with 5 parts of water, cooled by a mixture of ice and salt, until the liquid turns green; the oily layer which forms at the bottom of the retort is carefully separated from the water, and agitated in a freezing mixture with small portions of mercuric oxide, to remove the excess of chlorine and hydrocyanic acid, after which it is rectified from calcic chloride (Gautier, *Bull. Soc. Chem.*, v. 403). A very mobile colourless liquid, with an excessively irritating odour, is thus obtained, which boils at 12·6° (54·7° F.); when cooled to 7° (19·4° F.) it is converted into a crystalline mass.

The gaseous chloride of cyanogen obtained by passing a current of chlorine into a retort containing a mixture of powdered mercuric cyanide and water cooled to 0° (32° F.) by immersion in ice, and subsequently heating the solution, is merely the vapour of the liquid chloride, which may easily be condensed by a suitable refrigerating mixture. It dissolves freely in alcohol and ether,—less readily in water.

CYANURIC CHLORIDE or *Solid Chloride of Cyanogen*, $C_3N_3Cl_3 = 184·5$.—The vapour of this compound is three times as dense as that of the liquid chloride. It may be prepared by decomposing concentrated hydrocyanic acid by exposing it in a glass vessel with an excess of dry chlorine to the direct rays of the sun, or by passing a gentle current of chlorine into a solution of 1 part of hydrocyanic acid in 4 of dry ether. It is also formed when cyanuric acid is distilled with phosphoric pentachloride. Cyanuric chloride crystallizes in white needles; it is but sparingly soluble in water, although it is freely taken up by alcohol and ether.

(1136) BROMIDES OF CYANOGEN.—*Cyanic Bromide*, CNBr or CyBr = 106, may be prepared by distilling a mixture of bromine and mercuric cyanide, or by passing bromine vapour into a mixture of 1 part of hydrocyanic acid with 4 of water. It is very volatile, and sublimes readily in glistening colourless needles. Its vapour, like that of the chloride, is very pungent, exciting a copious flow of tears. When heated to 130°—140° (266°—284° F.) for six or eight hours, either alone or dissolved in anhydrous ether, it is converted into the polymeric modification $C_3N_3Br_3$, corresponding to the solid cyanuric chloride. *Cyanuric bromide* is insoluble in alcohol and benzene, and nearly insoluble in ether; it melts at above 300° (572° F.), and boils at a still higher temperature.

CYANIC IODIDE or *Iodide of Cyanogen*, CNI or CyI = 153, crystallizes in long colourless needles, which are readily volatile. It may be prepared by gently heating a mixture of iodine and mercuric cyanide, or by adding iodine to a concentrated solution of potassic cyanide in equal molecular weights, extracting the cyanic iodide by agitation with ether, evaporating the ethereal solution, and subliming.

(1137) CYANIC ACID OR HYDRIC CYANATE: HCNO = 43.—Cyanic acid may be prepared by distilling the polymeric body, *cyanuric acid*, $H_3C_3N_3O_3$ (1145), 1 molecule of which contains exactly the same elements as 3 molecules of cyanic acid. When this compound is sealed up in a bent glass tube, one limb of which is kept cool whilst heat is applied to the cyanuric acid in the other limb, a limpid, colourless liquid distils over and is condensed. The cyanuric acid is thus wholly converted into pure cyanic acid.

Cyanic acid has an extremely pungent odour, and is very volatile; its vapour attacks the eyes powerfully, and when liquid it acts as a powerful caustic if dropped upon the skin. It is, however, impossible to preserve this compound, for in the course of a few hours it changes spontaneously, with development of heat, into a white enamel-like mass, which is permanent in the air and insoluble in water; to this body the name of *cyamelid* has been given; it has the same centesimal composition as cyanuric and cyanic acids, with which it is polymeric.

Cyamelid may also be obtained by triturating potassic cyanate with crystallized oxalic or tartaric acid, and washing out the soluble salt of potassium. It may be reconverted by heat into cyanic acid; if boiled with a solution of potassic hydrate it gradually forms potassic cyanurate; sulphuric acid decomposes it with evolution of carbonic anhydride, whilst ammonic sulphate is produced.

A solution of cyanic acid in water quickly decomposes into ammonic carbonate and urea, CON_2H_4:

$$HCNO + OH_2 = CO_2 + NH_3; \text{ and } HCNO + NH_3 = CON_2H_4.$$

(1138) Potassic Cyanate, $KCNO = 81{\cdot}1$.—If cyanogen gas be passed into an alkaline solution, a change ensues somewhat analogous to that which occurs under similar circumstances with chlorine, cyanide and cyanate of the metal being produced: $C_2N_2 + 2KHO = KCN + KCNO + OH_2$. If potassic carbonate be heated in cyanogen gas, a mixture of potassic cyanide and cyanate is formed, whilst carbonic anhydride is set free:

$$K_2CO_3 + C_2N_2 = KCN + KCNO + CO_2.$$

Potassic cyanate, however, is more readily prepared by fusing potassic cyanide in a crucible, and adding litharge (plumbic oxide) in small quantities, until the oxide ceases to be decomposed: $KCN + PbO = KCNO + Pb$. The cyanate is easily separated from the reduced lead and the excess of plumbic oxide, which, from their superior density, sink through the melted mass to the bottom. The cyanate may be purified by solution in boiling alcohol, from which it crystallizes on cooling in deliquescent plates. Another, but less productive, method of preparing potassic cyanate consists in heating an intimate mixture of 2 parts of thoroughly dried potassic ferrocyanide with 1 part of finely powdered anhydrous black oxide of manganese: the mixture is placed upon a sheet-iron plate and heated to dull redness, the mass being kept constantly stirred. The oxidation of the cyanide is effected partly at the expense of the oxygen in the oxide of manganese, partly of that in the atmosphere. When the combustion has ceased, potassic cyanate may be dissolved out of the residue with hot alcohol.

Potassic cyanate, if kept dry, may be preserved without change; but so unstable is cyanic acid, that on attempting to prepare it from potassic cyanate by the addition of an excess of sulphuric or any other strong acid, traces of it only are obtained:

a brisk effervescence ensues—each molecule of the cyanic acid assimilates the elements of water, and is almost entirely resolved into 1 molecule of ammonia, which remains in combination with the acid employed in decomposing the cyanate, and one of carbonic anhydride, which escapes with effervescence:

$$\underset{\text{Potassic cyanate.}}{2KCNO} + 2OH_2 + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Ammonic sulphate.}}{(NH_4)_2SO_4} + \underset{\text{Potassic sulphate.}}{K_2SO_4} + 2CO_2.$$

POTASSIC ISOCYANATE, KCNO.—This compound, which is isomeric with potassic cyanate, is formed by the action of potassic hydrate on paracyanogen, on fusing paracyanogen with potassic cyanide, and also when a current of the vapour of cyanic chloride is passed into a concentrated aqueous solution of potassic hydrate. Melms finds that when the ordinary potassic cyanate is heated with cyanic iodide, the former is entirely converted into the isocyanate, although the iodide undergoes no change. Potassic isocyanate crystallizes from alcohol in long thin needles, very different in appearance from the ordinary cyanate; after its solution has been submitted to the long-continued action of an alkaline hydrate, the addition of argentic nitrate, after neutralization with nitric acid, produces a white precipitate of *silver dicyanimide*, C_2N_3Ag (Bannow, *Deut. chem. Ges. Ber.*, iv. 253).

AMMONIC CYANATE, NH_4CNO, is formed when the vapour of cyanic acid is allowed to come into contact with dry ammonia. It is a snow-white crystalline powder, which, on being boiled with water, is converted into the isomeric body *urea*.

Solutions of the soluble cyanates give white precipitates with solutions of mercurous salts as well as with those of the salts of lead and of silver; they yield no precipitate with solution of mercuric chloride, or with the solutions of salts of iron or tin. With cupric nitrate they give a greenish-brown precipitate, and with auric chloride a brown precipitate.

(1139) SULPHOCYANATES OR THIOCYANATES, *Rhodanates.*—When potassic cyanide is fused with sulphur, or even when a solution of the cyanide is boiled with flowers of sulphur, the two bodies enter into combination, and *potassic sulphocyanate*, KCNS, is formed; this compound is also readily prepared by heating to dull redness in a covered crucible an intimate mixture of 3 parts of anhydrous potassic ferrocyanide, 2 of sulphur, and 1 of potassic carbonate. The melted mass when cold should be treated with boiling-water, to separate the ferrous sulphide formed in the operation, and the filtered liquid evaporated: on cooling, striated prismatic crystals of potassic sulphocyanate will be deposited, which may be purified by recrystallization from alcohol; or the sulphocyanate may be obtained directly from the fused mass by treatment with alcohol.

Potassic Sulphocyanate, $KCNS = 97{\cdot}1$, is anhydrous, but very deliquescent, dissolving readily in water with considerable depression of temperature; it is also very soluble in hot alcohol. It fuses readily when heated. It is not poisonous.

Potassic Isosulphocyanate, $KCNS$, prepared by acting on persulphocyanic acid (1142) with an alcoholic solution of potassic hydrate, is a yellow granular mass, which becomes white when boiled with alcohol. It is very soluble in water, but almost insoluble in alcohol, and crystallizes from dilute alcohol in tufts of needles. By long continued boiling of the aqueous solution it becomes partly converted into the ordinary sulphocyanate, and this change is immediately effected by fusing the dry salt. In its reactions with metallic salts it behaves very differently from the sulphocyanate, merely giving a brown colour with a solution of ferric chloride, which disappears on adding an excess of the latter. With argentic nitrate it yields a pale yellow precipitate almost insoluble in ammonia, whilst the ordinary sulphocyanate yields a white precipitate soluble in ammonia.

The sulphocyanates may be regarded as representatives of the cyanates, in which the oxygen of the latter salts has had its place supplied by sulphur, the decomposition of sulphocyanic acid by the aid of heat and acids resembling that of cyanic acid under similar circumstances; thus with dilute sulphuric acid it gives carbonic oxysulphide, cyanic acid yielding carbonic anhydride:

$$\underset{\text{Sulphocyanic acid.}}{HCNS} + H_2SO_4 + OH_2 = \underset{\text{Carbonic oxysulphide.}}{COS} + NH_4.HSO_4.$$

$$\underset{\text{Cyanic acid.}}{HCNO} + H_2SO_4 + OH_2 = \underset{\text{Carbonic anhydride.}}{CO_2} + NH_4.HSO_4.$$

Ammonic sulphocyanate, also, is converted into *thiourea*, CSN_2H_4, when heated, just as urea, CON_2H_4, is formed from ammonic cyanate during the evaporation of its solution.

The majority of the sulphocyanates are soluble both in water and in alcohol, and are distinguished by the production of an intense blood-red colour when their solutions are mixed with one of the ferric salts; if the red liquid be then acidulated with hydrochloric acid, and fragments of zinc added, sulphuretted hydrogen is disengaged, and the colour disappears, methylamine being formed amongst other products. Ferric sulphocyanate does not form crystals. *Plumbic sulphocyanate* is sparingly soluble; it is slowly deposited in brilliant anhydrous crystals when solutions of plumbic acetate and potassic sulphocyanate are mixed. Basic plumbic acetate gives a white precipitate. The sulphocyanates also give a white precipitate of *cuprous sulphocyanate*, $Cu_2(CNS)_2$, when added to a mixture of a ferrous salt with a cupric salt; with mercurous salts and with the salts of silver and of gold, they produce white precipitates.

AMMONIC SULPHOCYANATE, $NH_4CNS = 76$.—A considerable quantity of this salt is found in the hydrated ferric oxide employed in gas works for absorbing the sulphuretted hydrogen from the crude gas, and also in the ammonia liquor, which accounts for its presence in commercial ammonic sulphate. It may be prepared by treating carbonic bisulphide with aqueous ammonia in closed vessels, or with an alcoholic solution of ammonia, the reaction being: $CS_2 + 4NH_3 = NH_4.CNS + (NH_4)_2S$; also by adding hydrocyanic acid to ammonic sulphide. It forms colourless deliquescent plates, which melt at 159° (318·2° F.), and are very soluble both in water and in alcohol.

MERCURIC SULPHOCYANATE, $Hg(CNS)_2$, is obtained on adding a solution of potassic sulphocyanate to one of mercuric nitrate. It is soluble in excess of either salt, and crystallizes from its solution in boiling water in nacreous laminæ. When heated, it readily decomposes with strong intumescence, so that on applying a light to one point of a small heap of the salt, the action rapidly spreads through the mass, which swells up to many times its original bulk.

(1140) SULPHOCYANIC ACID, HCNS.—When dry mercurous sulphocyanate is heated in a current of sulphuretted hydrogen, mercurous sulphide is produced, and a colourless oily liquid which is *sulphocyanic acid.* This acid boils at 102° (215·6° F.); when cooled to —12° (10·4° F.), it solidifies to a radiated mass of six-sided prisms. It has a pungent odour, resembling that of acetic acid and a strong acid taste. It is a dangerous poison. In the concentrated state it soon undergoes decomposition into hydrocyanic and *persulphocyanic acid:*

$$3\,HCNS = HCN + C_2N_2S_3H_2.$$

Sulphocyanic acid may be obtained in solution by suspending the sulphocyanate of copper, mercury, or silver in water, and decomposing it by means of a current of sulphuretted hydrogen. When a dilute solution is boiled, it gradually undergoes decomposition, ammonia, carbonic bisulphide, and carbonic anhydride being formed; in a more concentrated state it is resolved into hydrocyanic and persulphocyanic acids; these changes occur more quickly in the presence of other acids.

(1141) SULPHOCYANIC ANHYDRIDE, *Cyanic or cyanogen sulphide,* $S(CN)_2 = SCy_2$, is best obtained by the action of cyanic iodide on argentic sulphocyanate in ethereal solution; it is also formed on heating argentic cyanide with sulphur chloride. It crystallizes in colourless rhombic laminæ, which melt at 65° (149° F.), but sublime at a much lower temperature. It is soluble in alcohol, ether, and carbonic bisulphide, but is decomposed by water with separation of a yellow substance; a solution of potassic hydrate converts it into potassic cyanate and sulphocyanate.

(1142) PERSULPHOCYANIC ACID, $C_2N_2S_3H_2$.—If a saturated solution of potassic sulphocyanate be mixed with 8 or 10 times its weight of concentrated hydrochloric acid, it is decomposed, hydrocyanic acid is evolved, and the solution becomes semi-solid from the separation of the so-called *persulphocyanic acid,* in crystalline needles. It may also be prepared by mixing a solution of ammonic sulphocyanate in its own weight of water with 3 vols. of sulphuric acid of sp. gr. 1·34. Persulphocyanic acid dissolves in 420 parts of boiling water, and as the solution cools it is deposited in beautiful orange-coloured needles. Its solution yields a yellow precipitate with argentic nitrate; with potassic hydrate it yields potassic isocyanate. (*See Thiourea.*)

(1143) PERSULPHOCYANOGEN, $C_3N_3S_3H$.—Solutions of sulphocyanic acid, and of the sulphocyanates are decomposed by nitric acid, and also by chlorine or bromine, a bright yellow precipitate of persulphocyanogen being produced, which is insoluble in water, alcohol, and ether. When heated with concentrated hydrochloric acid it is decomposed, yielding cyanuric acid, hydric sulphide, and hydric persulphide (Glutz, *Deut. chem. Ges. Ber.*, iii. 343):

$$C_3N_3S_3H + 3OH_2 = C_3N_3O_3H_3 + SH_2 + S_2H_2.$$

(1144) Dicyanic Acid, $C_2O_2N_2H_2$.—Schmitt states that this compound, which as yet has scarcely been examined, is formed by the action of carbonic oxychloride on urea:

$$CON_2H_4 + COCl_2 = C_2O_2N_2H_2 + 2HCl.$$

(1145) Cyanuric Acid, $C_3O_3N_3H_3$.—This polymeride of cyanic acid may be obtained in various ways. 1. By heating biuret, $C_2O_2N_3H_5$, with carbonic oxychloride, $COCl_2$, to 150° (302° F.). 2. By decomposing cyanuric chloride by prolonged boiling with water, or by dissolving it in hydrated alcohol; in the latter case the liquid becomes hot, hydrochloric acid is formed, and crystals of cyanuric acid are slowly deposited:

$$C_3N_3Cl_3 + 3OH_2 = C_3O_3N_3H_3 + 3HCl.$$

3. By the action of a current of dry chlorine upon fused urea:

$$6CON_2H_4 + 3Cl_2 = 2C_3O_3N_3H_3 + N_2 + 2HCl + 4NH_4Cl;$$

the ammonic chloride which is formed may be removed by washing with cold water, and the cyanuric acid crystallized from boiling water. 4. By decomposing urea hydrochloride by heat: if the compound formed by passing dry hydrochloric acid gas over powdered urea be heated to 145° (293° F.) in an oil bath, rapid decomposition occurs, and ammonic chloride sublimes; pure cyanuric acid may be obtained by crystallizing the residue from boiling water: $3CON_2H_5Cl = C_3O_3N_3H_3 + 3NH_4Cl$. 5. By heating urea beyond its fusing point until it has become converted into a dry greyish mass: when this residue, which consists of cyanuric acid, ammelide or melanuric acid, and biuret is dissolved in hot sulphuric acid, to which a small quantity of nitric acid has been added for the purpose of removing the colour, it is converted into cyanuric acid, which is deposited on diluting the liquid moderately with water. 6. By the destructive distillation of uric acid; cyanuric acid being one of the products obtained in this operation. 7. If cyamelide be heated with sulphuric acid until carbonic anhydride begins to be evolved, and the solution, as soon as it is cool, diluted with water, crystals of anhydrous cyanuric acid are deposited after some time.

Cyanuric acid is deposited from its aqueous solution in colourless rhombic prisms, $C_3O_3N_3H_3,2OH_2$, which are efflorescent. It is sparingly soluble in cold water, more freely so in boiling water, and is also somewhat soluble in boiling alcohol. When crystallized from hot hydrochloric or nitric acid, it is deposited in square-based anhydrous octahedra. By long boiling with concentrated acids it is decomposed into carbonic anhydride and ammonia. When crystallized cyanuric acid is distilled, it is converted into cyanic acid, but this, as already noticed, in a short time begins to undergo a spontaneous change into the white insoluble compound known as *cyamelide* (1137).

Most of the cyanurates are crystalline and sparingly soluble in water. Those which are produced even when the acid is mixed with a considerable excess of an alkali or alkaline earth, have only two of the three atoms of hydrogen displaced by the equivalent quantity of the metal. *Monopotassic cyanurate*, $C_3O_3N_3H_2K$, is deposited in anhydrous cubes, when acetic acid is added in small quantities at a time to a solution of potassic cyanate; three molecules of cyanic acid coalescing to form one molecule of the cyanurate:

$$\underset{\text{Potassic cyanate.}}{3\mathrm{CONK}} + \underset{\text{Acetic acid.}}{2\mathrm{HC_2H_3O_2}} = \underset{\text{Monopotassic cyanurate.}}{\mathrm{C_3O_3N_3H_2K}} + \underset{\text{Potassic acetate.}}{2\mathrm{KC_2H_3O_2}}.$$

When a solution of a salt of copper, after being saturated with ammonia, is mixed with a solution of cyanuric acid, a characteristic violet precipitate is formed, which is insoluble in cold water. *Diargentic cyanurate*, $C_3O_3N_3HAg_2$, and *triargentic cyanurate*, $C_3O_3N_3Ag_3$, are white crystalline substances, insoluble in water, but slightly soluble in dilute nitric acid.

(1146) *Constitution of Cyanic and Cyanuric Acids.*—Strictly speaking neither of these compounds can be considered as carbo-acids, since they cannot be represented by formula which contain the COOH group (1072). The only constitutional formulæ which we are able to assign to a substance having the composition CONH are as follows:

$$\mathrm{N'''}\left\{\begin{matrix}\mathrm{(CO)''}\\ \mathrm{H}\end{matrix}\right. \text{ or } \mathrm{H{-}N{=}C{=}O}; \text{ and } \mathrm{C^{iv}}\left\{\begin{matrix}\mathrm{N'''}\\ \mathrm{(OH)'}\end{matrix}\right. \text{ or } \mathrm{N{\equiv}C{-}O{-}H}.$$

It is probable that ordinary potassic cyanate is the potassium derivative of the first of these, NH.CO, which, as it is the imide of carbonic acid, is appropriately termed *carbimide;* whilst potassic isocyanate is derived from the second compound, NC.OH, which is the hydrate of cyanogen.

The constitution of cyanuric acid may be inferred from its formation from biuret. Schmit (*Journ. pr. Chem.* [2], v. 46) found that when this compound is heated with carbonic oxychloride *carbonyl-dibiuret* is first formed:

$$\underset{\text{Biuret.}}{2\mathrm{NH}\left\{\begin{matrix}\mathrm{CO.NH_2}\\ \mathrm{CO.NH_2}\end{matrix}\right.} + \mathrm{COCl_2} = \underset{\text{Carbonyl-dibiuret.}}{\mathrm{NH}\left\{\begin{matrix}\mathrm{CO.NH_2} & \mathrm{NH_2.CO}\\ \mathrm{CO.NH.CO.NH.CO}\end{matrix}\right\}\mathrm{NH}} + 2\mathrm{HCl};$$

which, by the further action of the chloride, is then converted into cyanuric acid:

$$NH\left\{\begin{matrix}CO.NH_2 \quad NH_2.CO\\ CO.NH.CO.NH.CO\end{matrix}\right\}NH + COCl_2 = NH\left\{\begin{matrix}CO.NH.CO.NH.CO\\ CO.NH.CO.NH.CO\end{matrix}\right\}NH + 2HCl.$$

Carbonyl-dibiuret. Dicarbonyl-dibiuret.

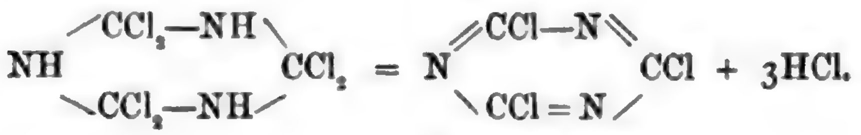
$$NH\left\{\begin{matrix}CO.NH.CO.NH.CO\\ CO.NH.CO.NH.CO\end{matrix}\right\}NH = 2NH\left\{\begin{matrix}CO.NH\\ CO.NH\end{matrix}\right\}CO.$$

Dicarbonyl-dibiuret. Cyanuric acid.

From this it would appear that cyanuric acid has the constitution represented by the formula $NH\left\{\begin{matrix}CO.NH\\ CO.NH\end{matrix}\right\}CO$, and the property it possesses in common with the true acids of exchanging hydrogen for a metal would be due to the presence of the imidogen group, NH. If this be taken as the constitutional formula of the acid the reaction with phosphoric pentachloride (1135) must be supposed to take place in the manner indicated by the following equations:

$$NH\left\{\begin{matrix}CO.NH\\ CO.NH\end{matrix}\right\}CO + 3PCl_5 = NH\left\{\begin{matrix}CCl_2.NH\\ CCl_2.NH\end{matrix}\right\}CCl_2 + 3POCl_3;$$

Cyanuric acid.



Cyanuric chloride.

(1147) CYANILIC ACID.—Sometimes during the preparation of cyanuric acid by boiling crude mellon with nitric acid, crystals of a compound which Liebig terms *cyanilic acid* are formed. It crystallizes in long, efflorescent prisms, and has the same composition as cyanuric acid, but is distinguished from it by its greater solubility.

(1148) FULMINATES.—When a solution of argentic or mercuric nitrate in an excess of nitric acid is heated with alcohol, a decomposition attended with a copious evolution of gas occurs, and a crystalline deposit of a metallic fulminate is formed. The fulminates are a class of salts polymeric with the cyanates, from which they are distinguished by the property they possess of detonating violently by percussion.

(1149) ARGENTIC FULMINATE, $C_2O_2N_2Ag_2$.—In order to prepare this salt 1 part of silver is dissolved at a gentle heat in 10 parts of nitric acid of sp. gr. 1·36, and the solution poured into 20 parts of alcohol of sp. gr. 0·840. On the application of a very gentle heat, an appearance of ebullition commences, the liquid becomes turbid, and, on cooling, deposits the crystallized fulminate, which may be washed with cold water, and dried at a very gentle heat. During the preparation of the salt, oxides of nitrogen, mixed with vapours of ethylic nitrate, and of aldehyde, as well as of acetic and formic acids, are liberated, and the solution is found to contain oxalic acid.

Argentic fulminate may also be obtained by passing nitrous anhydride into an alcoholic solution of argentic nitrate. In this case crystals of the fulminate are deposited without any disengagement of gas during the reaction illustrated by the following equation:

$$\underset{\text{Alcohol.}}{C_2H_6O} + N_2O_3 + 2AgNO_3 = \underset{\text{Argentic fulminate.}}{C_2O_2N_2Ag_2} + 2OH_2 + 2HNO_3.$$

Argentic fulminate is sparingly soluble in cold water, but soluble in 36 parts of boiling water. Its most remarkable property is its extremely explosive nature. When quite dry, a blow, or even very slight friction between two hard bodies, is sufficient to cause its decomposition, attended with a detonation of extraordinary violence. Even when moist, or under water, pressure with a hard body will often produce a similar effect. In like manner, an explosion is caused by the addition of a drop of sulphuric acid, the contact of gaseous chlorine, or an elevation of temperature somewhat above 130° (266° F.). It is decomposed with effervescence by dilute sulphuric acid, oxalic acid and ammonia being formed, and hydrocyanic acid liberated. Dilute hydrochloric acid also decomposes it, the silver being precipitated wholly in the form of chloride. Sulphuretted hydrogen converts the salt into argentic sulphide, and liberates cyanic acid, which, if the sulphuretted hydrogen be in excess, is converted into sulphocyanic acid.

Solutions of the alkaline chlorides, even when employed in excess, precipitate only one-half of the silver in the form of chloride, producing double salts, such as *argentic potassic fulminate*, $C_2O_2N_2KAg$ (?), which is a highly explosive compound, crystallizing in elongated brilliant leaflets.

A *hydric argentic fulminate*, $C_2O_2N_2AgH$ (?), may be obtained in the form of a white powder by the cautious addition of nitric acid to one of these double fulminates. It is soluble in boiling water, and crystallizes on cooling. If boiled with mercuric oxide it dissolves the oxide, forming a mercuric diargentic fulminate $(C_2O_2N_2)_2Ag_2Hg$.

If a solution of argentic fulminate be boiled with metallic mercury, or copper, the whole of the silver is precipitated, and a fulminate of mercury or of copper is formed.

(1150) MERCURIC FULMINATE, $C_2O_2N_2Hg,xOH_2$.—The best method of preparing this salt, according to Liebig, consists in dissolving 3 parts of mercury in 36 of nitric acid, of sp. gr. 1·34, without the aid of heat, in a flask capable of containing 18 times the bulk of the acid. The solution is then to be poured into a large vessel containing 17 parts of alcohol, of sp. gr. 0·830, and immediately retransferred to the flask which is still full of nitrous vapours, and with which it should be agitated to effect their absorption. In a few minutes an effervescence commences, which becomes very violent and is attended with a deposit of metallic mercury; this, however, is gradually redissolved. The reaction must be moderated by the gradual addition of 17 parts more of alcohol; and, on cooling, crystals of the fulminate, amounting to 4·6 parts, are deposited. The reaction is attended with the formation of the same products as when silver is used. Glycolic acid is also found in the mother liquor.

Mercuric fulminate forms white silky needles, which have a metallic sweetish taste. It is sparingly soluble in cold water, but much more soluble in boiling water, or in a solution of ammonia. It may be handled without much danger while moist, but when dry if it be exposed to the electric spark, or heated to about 180° (356° F.), it explodes; and if it be struck by a hard body, or touched with concentrated sulphuric or with nitric acid, detonation occurs, but the suddenness of the explosion is decidedly less than that of argentic fulminate. The priming of the ordinary percussion cap consists of a mixture of 1 part of mercuric fulminate with 6 parts of nitre, or of a mixture of 3 parts of the fulminate, 5 of potassic chlorate, 1 of sulphur, and 1 of ground glass. It is applied in the form of a dry powder, and is made to adhere to the cap by the subsequent application of a drop of shell-lac varnish.

When either zinc or copper is boiled with mercuric fulminate suspended in water, the whole of the mercury is displaced by the metal which is employed, and fulminate of zinc, or of copper, is formed. No fulminates are known in which both atoms of hydrogen are displaced by the metal of an alkali or an alkaline earth. If argentic or mercuric fulminate be mixed with a solution of potassic hydrate in excess, only one half of the silver or mercury is precipitated in the form of oxide, leaving a potassic argentic, or potassic mercuric fulminate in solution.

The constitution of the fulminates will be discussed when the cyano-derivatives of the hydrocarbon of the C_nH_{2n+2} series, or paraffins, are described.

(1151) **Fulminuric Acid**; *Isocyanuric Acid*, $C_3O_3N_3H_3$.—This compound was discovered at about the same time by Liebig and by Schischkoff. It is isomeric or polymeric with cyanuric acid, but contains only one atom of hydrogen displaceable by a metal. The fulminurates are obtained by boiling one of the fulminates, such as mercuric fulminate, with a solution of a soluble chloride. When mercuric fulminate is thus boiled with potassic chloride, it is gradually dissolved, and a yellow compound containing mercury is separated; during the first part of the operation the liquid appears to be turbid, but as soon as this appearance ceases it is filtered, and on being evaporated it yields brilliant crystals of potassic fulminurate. The general result of the reaction may be thus represented:

$$\underset{\text{Fulminic acid.}}{2C_2O_2N_2H_2} + OH_2 = \underset{\text{Fulminuric acid.}}{C_3O_3N_3H_3} + CO_2 + NH_3.$$

The fulminurates crystallize with great facility; they possess a high lustre, and exert a great dispersive power on light. They are decomposed by heat with a feeble explosion; when submitted to electrolysis they furnish carbonic anhydride, cyanogen, ammonia, and a nitrate.

It thus appears (supposing isolated fulminic acid to be capable of existing, and cyanilic acid to be a distinct compound) that not less than 7 compounds polymeric with cyanic acid might be produced—namely:

Cyanic acid . . .	CONH.
Dicyanic acid . . .	$C_2O_2N_2H_2$?.
Cyanuric acid. . .	$C_3O_3N_3H_3$.
Cyamelid	xCONH.
Cyanilic acid . . .	$C_3O_3N_3H_3$?.
Fulminic acid . .	$C_2O_2N_2H_2$?.
Fulminuric acid . .	$C_3O_3N_3H_3$?.

CHAPTER V.

THE HYDROCARBONS AND THEIR HALOID, NITRO, AND CYANO DERIVATIVES.

§ I. *Hydrocarbons of the* C_nH_{2n+2} *series. The Paraffins*;—§ II. *Hydrocarbons of the* C_nH_{2n} *series. The Olefines*;—§ III. *Hydrocarbons of the* C_nH_{2n-2} *series*;—§ IV. *Hydrocarbons of the* C_nH_{2n-4} *series. The Terpenes*; — § V. *Hydrocarbons of the* C_nH_{2n-6} *series*;—§ VI. *Hydrocarbons of the* C_nH_{2n-8} *series*;—§ VII. *Hydrocarbons of the* C_nH_{2n-10} *series*;—§ VIII. *Hydrocarbons of the* C_nH_{2n-12} *series*;—§ IX. *Hydrocarbons of the* C_nH_{2n-14} *series*;—§ X. *Hydrocarbons of the* C_nH_{2n-16} *series*;—§ XI. *Hydrocarbons of the* C_nH_{2n-18} *series*;—§ XII. *Hydrocarbons of the* C_nH_{2n-20} *series*;—§ XIII. *Hydrocarbons of the* C_nH_{2n-22} *series*;—§ XIV. *Hydrocarbons of the* C_nH_{2n-24} *series*;—§ XV. *Hydrocarbons of the* C_nH_{2n-26} *series*;—§ XVI. *Hydrocarbons of the* C_nH_{2n-30} *series*;—§ XVII. *Hydrocarbons of the* C_nH_{2n-32} *series.*

§ I. HYDROCARBONS OF THE C_nH_{2n+2} SERIES. THE PARAFFINS.

(1152) THE name paraffin (*parum affinis*) was first applied to a crystalline solid obtained by Reichenbach in 1830, from wood tar, and since largely manufactured by the distillation of cannel coal and bituminous shales; the liquid oil produced at the same time naturally took the name of 'paraffin oil.' Both these substances consist chiefly of mixtures of hydrocarbons having the general formula C_nH_{2n+2}, and the term paraffin as suggested by Watts, is now applied to the entire series.

The members of this large group of hydrocarbons homologous with methane or marsh gas, CH_4, are characterized by their chemical indifference, showing not the slightest tendency to enter into combination, and exhibiting to the fullest extent the properties of saturated molecules. They are scarcely acted on at the ordinary temperature even by fuming nitric acid, although they are easily oxidized by long continued boiling with dilute nitric acid, yielding principally carbonic anhydride and a mixture of solid and volatile acids of the acetic and succinic series with nitriles; similar products, with the exception of the nitriles, are obtained by treatment with a mixture of dilute sulphuric acid and potassic dichromate. From the experiments of Berthelot, it would seem that the action of potassic permanganate is but feeble, since he found that it required two months' treatment with that reagent to completely oxidize a few decigrams of the paraffin hexane. They are not attacked by a dilute solution of hypochlorous acid. The action of chlorine and bromine on the paraffins gives rise to substitution products. They are not dissolved by concentrated sulphuric acid, neither do they combine with sulphuric anhydride.

Hoffmann has proposed that the termination *ane* should be employed to distinguish the members of this series, a nomenclature now generally adopted. The first four, methane, ethane, propane, and tetrane are gaseous at the ordinary temperature; the next higher homologues are colourless mobile liquids whose density and boiling point gradually increase as the number of carbon atoms in the molecule becomes greater, whilst the highest members are crystalline solids.

(1153) METHODS OF FORMATION OF THE PARAFFINS.—Although 'marsh gas,' CH_4, had long been known, the first member of the series which was prepared artificially was the octane, C_8H_{18}, obtained by Kolbe during the electrolysis of potassic valerate; subsequently a more general method of obtaining these bodies was discovered by Frankland, in the decomposition which the moniodoparaffins undergo when heated with zinc to a high temperature in sealed tubes.

1. *By the action of Nascent Hydrogen on Carbon Compounds.*—Berthelot, in his remarkable experiments on the action of hydriodic acid on organic bodies has found that all carbon com-

pounds if heated to 270°—280° (518°—536° F.) with a large excess of a concentrated aqueous solution of that acid of density 2·0 are converted into the corresponding saturated hydrocarbon containing the same number of carbon atoms as the original compound, or into mixtures of the paraffins lower in the series. Thus benzene, C_6H_6, is converted into hexane, C_6H_{14}, and toluene, C_7H_8, into heptane, C_7H_{16}, whilst naphthalene, $C_{10}H_8$, yields a mixture of decane, $C_{10}H_{22}$, hexane, C_6H_{14}, and octane, C_8H_{18}. Similarly, the haloid derivatives of the hydrocarbons, the alcohols, aldehydes and many acids are said to yield the corresponding paraffins by this method of treatment.

A very general and advantageous method of preparing pure paraffins is to act upon their monohaloid derivatives with a mixture of zinc and hydrochloric acid; the action is often facilitated by dissolving the haloid derivatives in alcohol:

$$Zn + 2HCl = H_2 + ZnCl_2;$$
$$C_nH_{2n+1}Cl + H_2 = C_nH_{2n+2} + HCl.$$
$$\underset{\text{Chloropropane.}}{C_3H_7Cl} + H_2 = \underset{\text{Propane.}}{C_3H_8} + HCl.$$

A similar effect is produced by heating the monohaloid derivatives of the paraffins with zinc and water to 200° (392° F.):

$$C_nH_{2n+1}I + Zn + OH_2 = C_nH_{2n+2} + ZnIOH.$$
$$\underset{\text{Iodopentane.}}{C_5H_{11}I} + Zn + OH_2 = \underset{\text{Pentane.}}{C_5H_{12}} + \underset{\text{Zincic iodohydrate.}}{ZnIOH.}$$

Gladstone and Tribe have recently shown (*Journ. Chem. Soc.*, 1873, 445, 678, 961), that this decomposition takes place at a much lower temperature, in many cases at the ordinary temperature, if the zinc be coated with spongy copper by immersing it in a dilute solution of cupric sulphate. Alcohol may also be employed in place of water.

2. *From Organo-metallic Compounds.*—Water acts with explosive violence on the zinc organo-metallic compounds giving rise to a paraffin:

$$Zn(C_nH_{2n+1})_2 + 2OH_2 = 2C_nH_{2n+2} + ZnH_2O_2$$
$$\underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} + 2OH_2 = \underset{\text{Ethane.}}{2C_2H_6} + ZnH_2O_2.$$

3. *By the action of Alkaline Hydrates on Acids.*—Paraffins are also produced when a mixture of a sodic salt of an acid of the acetic or succinic series is heated with excess of an alkaline hydrate:—

$$C_nH_{2n+1}.COONa + NaHO = C_nH_{2n+2} + Na_2CO_3.$$

$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + NaHO = \underset{\text{Methane.}}{CH_4} + Na_2CO_3.$$

$$C_nH_{2n}(COOK)_2 + 2KHO = C_nH_{2n+2} + 2K_2CO_3.$$

$$\underset{\text{Potassic suberate.}}{C_6H_{12}(COOK)_2} + 2KHO = \underset{\text{Hexane.}}{C_6H_{14}} + 2K_2CO_3.$$

In this reaction, however, owing to the high temperature required, the product is usually more or less contaminated with the products of secondary decomposition.

4. *By the Electrolysis of Acids.*—In the electrolysis of a solution of an alkaline salt of an acid of the acetic series, such as acetic acid, hydrogen and potassic hydrate make their appearance at the negative electrode, whilst carbonic anhydride and a paraffin are found at the positive electrode; thus:

$$2C_nH_{2n+1}COOK + 2OH_2 = H_2 + 2KHO + 2CO_2 + C_{2n}H_{4n+2} \text{ or}$$

C_mH_{2m+2} where $m = 2n$.

$$\underset{\text{Potassic acetate.}}{2CH_3COOK} + 2OH_2 = H_2 + 2KHO + 2CO_2 + \underset{\text{Ethane.}}{C_2H_6}.$$

5. *By the action of Metals on the Monohaloid Derivatives of the Paraffins.*—The majority of the moniodoparaffins when acted upon by metallic sodium yield a paraffin containing twice as many carbon atoms in the molecule as the moniodoparaffin:

$$2C_nH_{2n+1}I + 2Na = C_{2n}H_{4n+2} + 2NaI.$$

$$\underset{\text{Iodotetrane.}}{2C_4H_9I} + 2Na = \underset{\text{Octane.}}{C_8H_{18}} + 2NaI.$$

If a mixture of two moniodoparaffins be taken, the number of carbon atoms in the molecule of the product is the sum of the carbon atoms in the two moniodoparaffins:

$$C_nH_{2n+1}I + C_mH_{2m+1}I + 2Na = C_{n+m}H_{2n+2m+2} + 2NaI.$$

$$\underset{\text{Iodethane.}}{C_2H_5I} + \underset{\text{Iodopentane.}}{C_5H_{11}I} + 2Na = \underset{\text{Heptane.}}{C_7H_{16}} + 2NaI.$$

It is often necessary to moderate the violence of the action of the sodium by the addition of an indifferent liquid such as ether.

When the moniodoparaffins are heated with zinc, a paraffin is obtained containing twice as many carbon atoms as there are in the molecule of the iodoparaffin, thus:

$$\underset{\text{Iodomethane.}}{2CH_3I} + Zn = \underset{\text{Ethane.}}{C_2H_6} + ZnI_2;$$

but, excepting when iodomethane (methylic iodide) is employed, the paraffin and olefine containing the same number of carbon atoms as the iodoparaffin are produced. It may be supposed that these are formed either by the splitting up of the higher paraffin at the moment of formation:

$$2C_nH_{2n+1}I + Zn = C_{2n}H_{4n+2} + ZnI_2;$$
$$C_{2n}H_{4n+2} = C_nH_{2n} + C_nH_{2n+2};$$

or, which is more probable, that portions of the iodoparaffin are so acted upon, that the corresponding paraffin and olefine are immediately produced:

$$C_nH_{2n+1}I + C_nH_{2n+1}I + Zn = C_nH_{2n} + C_nH_{2n+2} + ZnI_2;$$

the hydriodic acid withdrawn from one molecule by the action of the metal reacting together with the metal upon a second molecule of the iodoparaffin to produce the paraffin and zincic iodide. Mercury in a few instances behaves like zinc.

6. *By Destructive Distillation.*—Paraffins are also very often produced during the destructive distillation of organic substances, and occur therefore in wood and coal tar. Many shales, as well as boghead and cannel coal, yield comparatively large quantities of these hydrocarbons. They are also produced by the gradual decomposition of vegetable matter beneath the earth's surface, giving rise to the petroleum which is obtained in such enormous quantities from the oil wells of Pennsylvania and Canada.

(1154) *Constitution of the Paraffins.*—The paraffins, C_nH_{2n+2}, are frequently regarded as the hydrides of the positive radicles, C_nH_{2n+1}, of the methyl series; thus methane, CH_4, would be considered to be methylic hydride, $CH_3.H$, and ethane, C_2H_6, ethylic hydride, $C_2H_5.H$. This view of their constitution, suggested by their mode of formation from the zinc compounds by the action of water:

$$\underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} + 2OH_2 = \underset{\text{Ethylic hydride.}}{2C_2H_5.H} + ZnH_2O_2,$$

is apparently supported by the fact that the action of chlorine on methane and ethane gives rise to the compounds CH_3Cl and C_2H_5Cl identical with the methylic and ethylic chlorides obtained by the action of hydrochloric acid on the corresponding alcohols. The case, however, is different with the next member of the series, propane,

C_3H_8, which under similar circumstances gives rise to two isomeric compounds of the formula C_3H_7Cl, namely, α-chloropropane or propylic chloride, $CH_3.CH_2.CH_2Cl$, and β-chloropropane or isopropylic chloride, $CH(CH_3)_2Cl$, so that we should have to regard propane simultaneously as propylic hydride and isopropylic hydride: this objection applies with still greater force to the higher members of the series.

The homologues of methane are, according to the present state of our knowledge, most conveniently regarded as methane, in which one or more of the hydrogen atoms are replaced by positive radicles of the form C_nH_{2n+1}.* Thus ethane, C_2H_6, would be represented as methylmethane, $CH_3.CH_3$, or, regarding its formation from methylic iodide by the action of sodium or zinc:

$$\underset{\text{Methylic iodide.}}{2CH_3I} + Zn = \underset{\text{Ethane.}}{C_2H_6} + ZnI_2,$$

where the two methyl groups, CH_3, unite to form the group C_2H_6, as dimethyl. It must be remarked, however, that the two methyl groups have, on thus coalescing, as it were, lost their individuality, since they are not separable as are the constituent atoms of the hydrogen molecule, H_2. Thus, whereas the action of a molecule of chlorine gives rise to two molecules of hydric chloride when it acts upon a molecule of hydrogen: $H_2 + Cl_2 = 2HCl$, it does not produce two molecules of methylic chloride when it acts upon ethane (dimethyl): $(CH_3)_2 + Cl_2 = 2CH_3Cl$, but a single molecule of chlorethane or ethylic chloride: $CH_3.CH_3 + Cl_2 = CH_3.CH_2Cl + HCl$. The same may be said of the other homologues of methane.

The hypothesis that the homologous paraffins are thus derived from methane is especially convenient in practice to recal the methods of formation, and to distinguish between the numerous isomerides in the higher terms of the series: thus the name of ethylmethane, as applied to the hydrocarbon propane, C_3H_8, is at once suggestive of its formation by the action of sodium on an ethereal solution of methylic and ethylic iodide:

$$\underset{\text{Ethylic iodide.}}{C_2H_5I} + \underset{\text{Methylic iodide.}}{CH_3I} + 2Na = 2NaI + \underset{\text{Ethylmethane}}{CH_3.C_2H_5} \text{ or } \underset{\text{Propane.}}{C_3H_8}.$$

In like manner the terms diethyl, for the normal tetrane, and trimethylmethane for isotetrane, suggest not only that one is prepared from ethylic iodide, and that the other is related to

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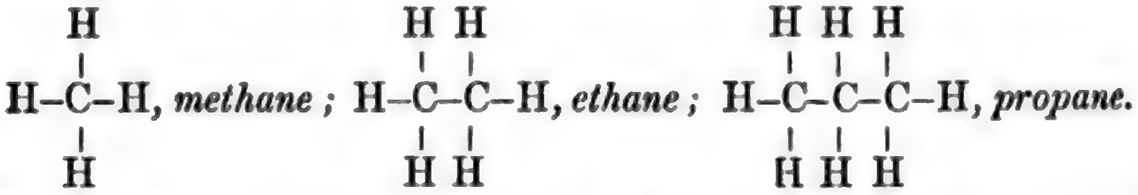
[*] The names given to these radicles are derived from those of the corresponding paraffins by changing the terminal *ane* into *yl*.

trimethylcarbinol, but also that the carbon atoms are not united in the same way, and therefore that they are isomeric.

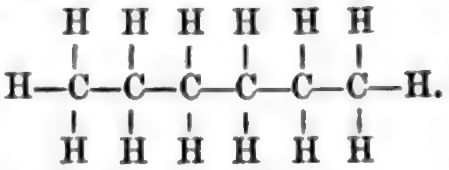
(1155) *Isomerism in the Paraffin Series.*—Of the first three members of the paraffin series, namely, methane, CH_4, ethane, C_2H_6, and propane, C_3H_8, no isomeric modifications exist. They exhibit the same physical and chemical properties in whatever way they may have been prepared, which is in accordance with what might have been expected from a consideration of their constitutional formulæ:



$$\mathrm{H-\overset{H}{\underset{H}{C}}-H}, \textit{ methane}; \quad \mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}, \textit{ ethane}; \quad \mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}, \textit{ propane}.$$

The paraffins, however, containing four or more carbon atoms admit of isomeric modifications, as will be shown when they are considered individually. Schorlemmer has proposed to divide these paraffins into four groups:—1. *Normal primary paraffins* in which each carbon atom is associated directly with at most two other carbon atoms as in *normal hexane*:

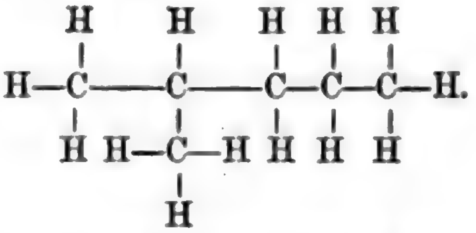
$C_6H_{14} = CH_3.CH_2.CH_2.CH_2,CH_2.CH_3$ or



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H.}$$

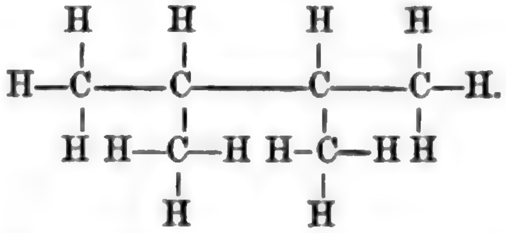
2. *Isoparaffins* in which one of the carbon atoms is associated with three others, or which contain the group isopropyl, $CH(CH_3)_2$, as *isohexane*:

$CH(CH_3)_2.CH_2.CH_2.CH_3$, or



3. Those which contain the isopropyl group twice, as *diisopropyl*:

$CH(CH_3)_2.CH(CH_3)_2$, or



4. Those in which one of the carbon atoms is associated with four others, as in ethyl-trimethyl-methane $C(C_2H_5)(CH_3)_3$. The accompanying table (pp. 134, 135) represents all the paraffins with whose properties we are acquainted arranged in four groups according to the method just described.

It will be seen that the boiling points of the normal paraffins are higher than those of their isomerides, and that the boiling points of the latter become lower, the more complex their structure; the hydrocarbon in group IV. boiling lower than the corresponding hydrocarbon in group III., and this again lower than that in II., whilst the normal paraffin has the highest boiling point. In group I. the increase of boiling point for each difference of CH_2 diminishes progressively, but appears to become constant when it is about 19° (66°·2 F.). In group II. the increase of boiling point for each difference of CH_2 is about 31° (55°·8 F.), and in group III. it is about 25° (45° F.), but these numbers must be regarded merely as rough approximations liable to alteration as our knowledge of these compounds in the pure state becomes increased. It will also be noticed that the specific gravity in the liquid state of the isomeric hydrocarbons varies in the same direction as the boiling point; the paraffin of higher boiling point having in most (probably in all) cases a higher specific gravity than that of the isomeric compound of lower boiling point.

(1156) **METHANE**; *Methylic hydride; Formene; Marsh gas; Light carburetted hydrogen* or *sub-carburetted hydrogen*: $CH_4 = 16$.—This gas, the lowest member of the paraffin series, has never been obtained by the direct union of its elements. According to Berthelot, however, it is formed in small quantities when a mixture of carbonic bisulphide vapour with hydric sulphide or with steam is passed over red hot copper turnings: $CS_2 + 2SH_2 + 2Cu_2 = CH_4 + 4CuS$.

Methane is one of the usual products of the destructive distillation of organic substances, such as wood, peat, and bituminous coal, and is consequently one of the principal constituents of coal-gas; it also occurs abundantly in many coal mines, bursting forth unexpectedly from the seams of coal, and blowing out from the fissure for many months together, as though escaping from under high pressure. These natural discharges of the gas the miners term "blowers." According to the experiments of Graham, the gas from the Newcastle coalfield is free from admixture with olefiant gas, hydrogen, carbonic oxide, and carbonic anhydride. It is also found issuing from the earth in many parts of Italy, Persia, China, and America. The holy fires of Baku on the Caspian Sea, which have been burning from time immemorial, are of this nature.

Preparation.—Pure methane can only be obtained by the decomposition of zincic methide by water: $Zn(CH_3)_2 + 2OH_2 = 2CH_4 + ZnO_2H_2$. When a large quantity is required it may be prepared by the process recommended by Persoz: 10¾ parts of baric

Table of Homologous

I.				II.			
Name.	**Formula.**	**Boiling point.**	**Specific gravity.**	**Name.**	**Formula.**	**Boiling point.**	**Specific gravity.**
Methane . .	CH_4						
Ethane . .	$C_2H_6 = \begin{matrix}CH_3\\ \mid\\ CH_3\end{matrix}$						
Propane . .	$C_3H_8 = \begin{matrix}CH_3\\ \mid\\ CH_2\\ \mid\\ CH_3\end{matrix}$						
Tetrane . . (Diethyl)	$C_4H_{10} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_2\\ \mid\\ CH_3\end{matrix}$	1°	·600 at 0°	Trimethylmethane . (Methylisopropyl)	$CH(CH_3)_3$	—15°	
Pentane . .	$C_5H_{12} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_3\\ \mid\\ CH_3\end{matrix}$	38°	·628 at 17°	Ethyldimethylmethane . . . (Ethylisopropyl)	$\begin{matrix}CH(CH_3)_2\\ \mid\\ C_2H_5\end{matrix}$	30°	·626 at 17°
Hexane . . (Dipropyl)	$C_6H_{14} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_4\\ \mid\\ CH_3\end{matrix}$	71°	·669 at 16°	Propyldimethylmethane . . . (Ethylisobutyl)	$\begin{matrix}CH(CH_3)_2\\ \mid\\ C_3H_7\end{matrix}$	62°	·701 at 0°
Heptane . .	$C_7H_{16} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_5\\ \mid\\ CH_3\end{matrix}$	99°	·699 at 15°	Triethylmethane . Tetryldimethylmethane . . . (Ethylisoamyl)	$CH(C_2H_5)_3$ $\begin{matrix}CH(CH_3)_2\\ \mid\\ C_4H_9\end{matrix}$	96° 91°	·689 at 27° ·683 at 18°·4
Octane . . . (Dibutyl)	$C_8H_{18} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_6\\ \mid\\ CH_3\end{matrix}$	124°	·703 at 17°	—	—	—	—
Nonane . .	$C_9H_{20} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_7\\ \mid\\ CH_3\end{matrix}$	148°	·728 at 13°·5	—	—	—	—
Decane . .	$C_{10}H_{22} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_8\\ \mid\\ CH_3\end{matrix}$	166–168°	·739 at 13°·5	—	—	—	—
Endecane . .	$C_{11}H_{24} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_9\\ \mid\\ CH_3\end{matrix}$	180–184°	·765 at 16°				
Dodecane . . (Dihexyl)	$C_{12}H_{26} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_{10}\\ \mid\\ CH_3\end{matrix}$	202°	·774 at 17°				
Tridecane . .	$C_{13}H_{28}$	216–218°	·792 at 20°				
Tetradecane .	$C_{14}H_{30}$	236–240°	—				
Pentadecane .	$C_{15}H_{32}$	258–262°	·825 at 16°				
Hexdecane . (Dioctyl)	$C_{16}H_{34} = \begin{matrix}CH_3\\ \mid\\ (CH_2)_{14}\\ \mid\\ CH_3\end{matrix}$	278°	solid melts at 21°				

and Isomeric Paraffins.

III.				IV.			
Name.	Formula.	Boiling point.	Specific gravity.	Name.	Formula.	Boiling point.	Specific gravity.
				Tetramethylmethane . .	$C(CH_3)_4$	9°·5	—
Diisopropyl .	$CH(CH_3)_2$ | $CH(CH_3)_2$	58°	·670 at 17°	Ethyltrimethylmethane . .	$C(C_2H_5)(CH_3)_3$	43°-48°	—
—	—	—	—	Diethyldimethylmethane . .	$C(C_2H_5)_2(CH_3)_2$	86°-87°	·696 at 21°
Diisobutyl . .	$CH(CH_3)_2$ | $(CH_2)_2$ | $CH(CH_3)_2$	110°	·698 at 16°				
Isobutylisoamyl	$CH(CH_3)_2$ | $(CH_2)_3$ | $CH(CH_3)_2$	132°	·724 at 0°				
Diisoamyl . .	$CH(CH_3)_2$ | $(CH_2)_4$ | $CH(CH_3)_2$	158°	·727 at 14°				

hydrate and 10⅓ of anhydrous sodic acetate are very intimately mixed, and heated over a charcoal fire, or gas stove, in a Florence flask, coated with a luting of fire-clay made into a paste with a solution of borax. The flask is fitted with a cork and bent tube, and the gas is passed first through a solution of sodic hydrate and afterwards through concentrated sulphuric acid: it may be collected over water in the usual way:

$$\underset{\text{Sodic acetate.}}{2CH_3.CO_2Na} + \underset{\text{Baric hydrate.}}{BaO_2H_2} = \underset{\text{Methane.}}{2CH_4} + \underset{\text{Baric carbonate.}}{BaCO_3} + \underset{\text{Sodic carbonate.}}{Na_2CO_3}.$$

A mixture of 2 parts of potassic hydrate and 3 of quicklime may be substituted for baric hydrate. The most convenient method, however, is to heat a mixture of 1 part of sodic acetate either with 3 of soda-lime or, as recommended by Schorlemmer, with 2 or 3 parts of a mixture of equal weights of anhydrous sodic carbonate and dry slaked lime, in a copper flask provided with a delivery tube.

The gas is also easily procured (mingled with nitrogen and carbonic anhydride), as a result of the decomposition of vegetable matter contained in the mud of stagnant pools; hence its name of *marsh gas*. In order to collect the gas from this source a bottle may be filled with water, inverted in the pool, and having fastened a funnel in the neck of the bottle, the mud beneath is stirred with a stick; the gas then rises into the bottle in bubbles.

Properties.—Methane is a colourless, inodorous, and tasteless gas, scarcely soluble in water, but soluble in alcohol to a small extent: not injurious to life if diluted with air. It does not support combustion, but is itself inflammable, and burns with a yellow luminous flame. By passing through it a continued succession of electric sparks, or by sending it through tubes heated to whiteness, it is decomposed: its carbon is deposited, and a volume of hydrogen, double that of the gas employed, is set at liberty.

Methane requires twice its volume of oxygen for complete combustion. Six volumes of the mixed gases after detonation are condensed into 2 volumes; they yield 2 volumes of carbonic anhydride, and 4 volumes of steam which are condensed. Now carbonic anhydride contains its own bulk of oxygen; it therefore represents 2 of the 4 volumes of oxygen which have disappeared, whilst the rest of the oxygen has united with 4 volumes of hydrogen and formed water. Two volumes of methane must consequently contain 4 volumes of hydrogen, or 4 parts by weight, united with 12 parts of carbon, and its composition may be thus represented :

			By weight.			By vol.
Carbon	C	=	12 or	75	...	?
Hydrogen	H_4	=	4	25	...	4
Methane	CH_4	=	16	100		2

Although chlorine has no action on methane in the dark, the mixture of the two gases explodes when exposed to the direct rays of the sun. In diffused daylight chlorine substitution compounds are formed, the principal product being monochloromethane or methylic chloride : with excess of chlorine it is ultimately converted into tetrachloromethane or carbonic tetrachloride, CCl_4, but if moisture be present, hydrochloric acid and carbonic anhydride are also formed :

$$CH_4 + 4Cl_2 + 2H_2O = CO_2 + 8HCl.$$

(1157) ETHANE, *Ethylic hydride* or *Dimethyl:* C_2H_6 or $CH_3.CH_3=30$.—This compound is a tasteless and odourless gas which has not as yet been liquefied. It is almost insoluble in water, but alcohol takes up more than its own bulk of the gas. A good method of preparing it consists in heating a mixture of equal parts of water and iodethane or ethylic iodide, C_2H_5I, with metallic zinc, in a sealed tube to a temperature of about 165° (329° F.) :

$$\underset{\text{Iodethane.}}{C_2H_5I} + Zn + OH_2 = \underset{\text{Ethane.}}{C_2H_6} + ZnIOH;$$

on breaking off the capillary extremity of the tube under water, the gas rapidly escapes, and may be collected in the usual way (Frankland). According to Gladstone and Tribe, the same action takes place with moderate rapidity even at the ordinary temperature when iodethane is added to the moist so-called 'zinc-copper couple,' which is prepared by immersing zinc foil in a dilute solution of cupric sulphate.

Ethane is obtained in a state of great purity by the action of water on zincic ethide :

$$\underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} + 2OH_2 = \underset{\text{Ethane.}}{2C_2H_6} + ZnH_2O_2;$$

or by heating methylic iodide with zinc or finely divided silver to 150° (302° F.) :

$$\underset{\text{Methylic iodide.}}{2CH_3I} + 2Ag = \underset{\text{Ethane.}}{C_2H_6} + 2AgI;$$

It may also be prepared by the electrolysis of a concentrated solution of potassic acetate:

$$2CH_3.COOK + OH_2 = C_2H_6 + CO_2 + K_2CO_3 + H_2.$$

The gas which is given off at the positive pole is a mixture of ethane and carbonic anhydride from which the latter may be removed by an alkaline hydrate.

The action of chlorine on ethane in diffused daylight gives rise, in the first place, to monochlorethane or ethylic chloride, and afterwards to higher chlorinated products.

(1158) **Propane**, *Propylic hydride*, or *Methyl-ethyl*: C_3H_8 or $CH_3.CH_2.CH_3 = 44$.—This compound occurs amongst the gases evolved from the petroleum springs in Pennsylvania, and also dissolved in the crude petroleum. It may be prepared from propylic or isopropylic iodide by the action of hydriodic acid, or of zinc and hydrochloric acid:

$$\underset{\text{Iodopropane.}}{C_3H_7I} + HI = \underset{\text{Propane.}}{C_3H_8} + I_2.$$

Propane is a gas which, at a low temperature, may be condensed to a colourless liquid. Alcohol dissolves about six times its volume of the gas. The action of chlorine on propane gives rise to two isomeric monochlorinated substitution compounds, namely *a-chloropropane* or *propylic chloride*, $CH_3.CH_2.CH_2Cl$, and *β-chloropropane* or *isopropylic chloride*, $CH_3.CHCl.CH_3$, besides higher chlorinated products.

(1159) **Tetrane** or **Butane**: $C_4H_{10} = 58$.—Two isomeric compounds having the formula C_4H_{10}, are capable of existing; both of these have been prepared and examined.

Normal tetrane, butane, butylic hydride, or *diethyl*: $CH_3.CH_2.CH_2.CH_3$, is found in crude petroleum. It may be prepared by heating a mixture of granulated zinc and ethylic iodide for two hours to a temperature of 150° (302° F.) in a strong sealed tube from which the air has been exhausted; the sides of the tube become coated with a white crystalline substance, consisting of zincic iodoethide, which is mixed with a colourless mobile liquid, equal in bulk to about half that of the ethylic iodide employed. This liquid is a mixture of tetrane with ethane and ethylene, the two latter the result of a secondary decomposition (p. 130). On opening the tube when cold, the liquid rapidly disappears and escapes in the gaseous form. The last portions, which consist of tetrane, may be condensed to a colourless liquid by means of a refrigerating mixture of ice and salt. Butane, mixed with ethane and ethylene, is also formed when ethylic iodide is exposed over mercury to the sun's rays, mercuric iodide being produced at the same time.

At the ordinary temperature butane is a colourless gas of sp. gr. 2·046 and possessing an ethereal odour. It burns with a highly luminous flame. The boiling point of the liquid is about 1° (33°·8 F.) Butane is insoluble in water, but freely soluble in alcohol, which dissolves about 18 times its bulk of the gas at 14° (57°·2 F.), giving it off again, however, when diluted with water.

Isobutane, pseudobutylic hydride, or *trimethylmethane*: $CH_3.CH(CH_3)_2$, or $CH(CH_3)_3$, is obtained by the action of zinc and water at a high temperature on tertiary butylic iodide:

$$CH_3.C(CH_3)_2I + Zn + OH_2 = CH_3.CH(CH_3)_2 + ZnIOH.$$

Some isobutene, C_4H_8, is also produced at the same time, but this may be removed by passing the mixed gases through bromine which only absorbs the isobutene. Isobutane is a gaseous body which at − 17° (1°·4 F.) may be condensed to a colourless liquid.

(1160) PENTANE: $C_5H_{12} = 72$.—The three compounds C_5H_{12} theoretically capable of existing are known.

Normal pentane, amylic hydride, or *butyl-methyl:* $CH_3.CH_2.CH_2.CH_2.CH_3$, or $CH_2(C_2H_5)_2$, is found in paraffin oil from cannel and boghead coal, and in large quantities in the lower boiling portions of American petroleum. It is a mobile colourless liquid boiling between 37° and 39° (98°·6 and 102°·2 F.)

Isopentane, isoamylic hydride, or *isobutyl-methyl:* $CH_3.CH(CH_3).CH_2.CH_3$, also occurs in petroleum and may be prepared by the following methods from the isoamylic compounds obtained from ordinary fermentation amylic alcohol.

1. By the action of zinc and water on the isoamylic iodide:

$$\underset{\text{Isoamylic iodide.}}{C_5H_{11}I} + Zn + OH_2 = \underset{\text{Isopentane.}}{2C_5H_{12}} + ZnIOH.$$

2. By the action of water on zinc isoamyl:

$$\underset{\text{Zinc isoamyl.}}{Zn(C_5H_{11})_2} + 2OH_2 = \underset{\text{Isopentane.}}{2C_5H_{12}} + ZnH_2O_2.$$

3. Together with amylene by heating zinc with isoamylic iodide:

$$\underset{\text{Isoamylic iodide.}}{2C_5H_{11}I} + Zn = \underset{\text{Isopentane.}}{C_5H_{12}} + \underset{\text{Amylene.}}{C_5H_{10}} + ZnI_2.$$

4. It is also formed together with amylene and its polymerides when isoamylic alcohol is distilled with zincic chloride.

The amylene formed in the above reactions may be removed from the mixture by means of fuming sulphuric acid, which dissolves the amylene and leaves the pentane.

Isopentane is a liquid of sp. gr. 0·626 at 17° (62°·6 F.) which boils at 30° (86° F.) and does not solidify at − 24° (− 11°·2 F.). It burns with a brilliant white flame, without smoke.

Tetramethyl-methane: $CH_3.C(CH_3)_3$, or $C(CH_3)_4$, is a colourless mobile liquid boiling at 9°·5 (49°·1 F.), produced by the action of zincic methide on tertiary butylic iodide:

$$\underset{\text{Butylic iodide.}}{CH_3.C(CH_3)_2I} + \underset{\text{Zincic methide.}}{Zn(CH_3)_2} = \underset{\text{Tetramethylmethane.}}{CH_3.C(CH_3)_3} + \underset{\text{Zincic iodomethide.}}{ZnICH_3};$$

and by the action of zincic methide on γ-dichloropropane (methylchloracetol):

$$\underset{\gamma\text{-Dichloropropane.}}{CH_3.CCl_2.CH_3} + Zn(CH)_3 = \underset{\text{Tetramethylmethane.}}{C(CH_3)_4} + ZnCl_2.$$

It solidifies to a crystalline mass at − 20° (− 4° F).

Frankland considers it probable that the *Eupion* which Reichenbach obtained during the rectification of the products from wood tar and from rape oil, is a pentane.

(1161) HEXANE: $C_6H_{14} = 86$.—Four of the five hexanes theoretically possible have been prepared and examined.

Normal hexane, Dipropyl, or *amyl-methyl:* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$, is a liquid of density 0·6630 at 17° (62°·6 F.) which boils at 71°·5 (160°·7 F.) It is formed from the secondary hexylic iodide obtained from mannite, by heating it with zinc and water, or by the action of zinc and dilute hydrochloric acid. It may also be obtained by decomposing an ethereal solution of normal propylic iodide with sodium at 150° (302° F.):

$$\underset{\text{Propylic iodide.}}{2CH_3.CH_2.CH_2I} + 2Na = \underset{\text{Hexane.}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3} + 2NaI;$$

or by exposing the iodide to the sun's rays in contact with mercury. It is found also in paraffin oil and in petroleum.

α-Isohexane, ethyl-isobutyl, or *isoamyl-methyl:* $CH_3.CH(CH_3).CH_2.CH_2.CH_3$.—On digesting a mixture of 40 parts of isobutylic iodide, 34 of ethylic iodide, and 11 of sodium, in a flask connected with a vertical condenser, so arranged that the volatilized products shall return constantly into the flask, a liquid is obtained which by fractional distillation yields α-isohexane boiling at 62° (143°·6 F.). It is a mobile colourless liquid of density 0·701 at 0° (32° F.).

β-Isohexane: $CH_3.CH_2.CH(CH_3).CH_2.CH_3$ has not yet been prepared.

Diisopropyl, or *tetramethyl-ethane:* $CH_3.CH(CH_3).CH(CH_3).CH_3$ is a liquid of sp. gr. 0·6769 at 10° (50° F.) obtained by the action of sodium on an ethereal solution of isopropylic iodide:

$$\underset{\text{Isopropylic iodide.}}{2CH_3.CH(CH_3)I} + Na_2 = \underset{\text{Diisopropyl.}}{CH_3.CH(CH_3).CH(CH_3).CH_3} + 2NaI.$$

This *γ-isohexane* boils at 58° (136°·4 F.).

δ-Isohexane, or *trimethyl-ethyl-methane:* $CH_3.CH_2.C(CH_3)_3$ or $C(C_2H_5)(CH_3)_3$, is formed by the action of zincic ethide on tertiary butylic iodide:

$$\underset{\substack{\text{Butylic}\\\text{iodide.}}}{C(CH_3)_3I} + \underset{\substack{\text{Zincic}\\\text{ethide.}}}{Zn(C_2H_5)_2} = \underset{\substack{\text{Trimethyl-ethyl-}\\\text{methane.}}}{C_2H_5.C(CH_3)_3} + \underset{\substack{\text{Zincic}\\\text{iodoethide.}}}{ZnIC_2H_5}.$$

It boils between 43° and 48° (109°·4 and 118°·4 F.).

(1162) HEPTANE: $C_7H_{16} = 100$.—Of the numerous possible hydrocarbons of the formula C_7H_{16} only three are at present known.

Normal Heptane: $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$, is found in paraffin oil and in Pennsylvanian petroleum; it is also formed on distilling azelaïc acid, $C_7H_{14}(COOH)_2$, with excess of baric oxide.

It is a liquid boiling at 99° (210°·2 F.).

Ethyl-isoamyl, or *dimethyl-butyl-methane:* $CH_3.CH_2.CH_2.CH_2.CH(CH_3)_2$, *α-Isoheptane.*—This is prepared by a method similar to that already described for α-isohexane by digesting a mixture of 60 parts of ethylic iodide and 70 of isoamylic iodide with 14 of sodium:

$$\underset{\text{Ethylic iodide.}}{CH_3.CH_2I} + \underset{\text{Isoamylic iodide.}}{CH(CH_3)_2.CH_2.CH_2I} + 2Na = \underset{\text{α-Isoheptane.}}{CH_3.CH_2.CH_2.CH_2.CH(CH_3)_2} + 2NaI.$$

By fractional distillation a liquid is obtained which boils at 91° (195°·8 F.), and has a density of 0·7069 at 0°.

Dimethyl-diethyl-methane: $CH_3.CH_2.C(CH_3)_2.CH_2.CH_3$, or $C(CH_3)_2(C_2H_5)_2$, is produced by the action of zincic ethide on γ-dichloropropane (methylchloracetol):

$$\underset{\text{γ-Dichloropropane.}}{CH_3.CCl_2.CH_3} + \underset{\text{Zincic ethide.}}{2Zn(C_2H_5)_2} = \underset{\text{Diethyl-dimethyl-methane.}}{CH_3.C(C_2H_5)_2.CH_3} + \underset{\text{Zincic chlorethide.}}{2ZnClC_2H_5}.$$

It is a colourless liquid boiling at about 86° (186°·8 F.). The heptane boiling at about 90° (194° F.), which accompanies normal heptane in petroleum, is perhaps dimethyl-diethyl-methane (Schorlemmer, *Chem. Soc. Journ.* 1873, 319.)

Triethyl-methane: $CH_3.CH_2.CH(CH_2.CH_3).CH_2.CH_3$ or $CH(C_2H_5)_3$, is a colourless liquid of density 0·689 at 27° (80°·6 F.), prepared by treating ethylic orthoformate with zincic ethide and sodium (Ladenburg):

$$\underset{\text{Ethylic orthoformate.}}{2CH(OC_2H_5)_3} + \underset{\text{Zincic ethide.}}{3Zn(C_2H_5)_2} + 6Na = \underset{\text{Triethyl-methane.}}{2CH(C_2H_5)_3} + \underset{\text{Sodic ethylate.}}{6NaOC_2H_5} + 3Zn.$$

It boils at 96° (204°·8 F.).

(1163) *Other Paraffins. Dibutyl:* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$.—This, the normal octane, occurs in petroleum and paraffin oil, and may be prepared in the usual way from normal octylic iodide, or by the action of sodium on normal butylic iodide, $CH_3.CH_2.CH_2.CH_2I$. It is also obtained from methyl-hexyl-carbinol, and by distilling potassic sebate with excess of potassic hydrate: $K_2C_{10}H_{16}O_4 + 2KHO = C_8H_{18} + 2K_2CO_3$. It has a density of 0·7032 at 17° (62°·6 F.), and boils at 123°—125° (253°·4—257° F.). Its isomeride, *diisobutyl:* $CH_3.CH(CH_3).CH_2.CH_2.CH(CH_3).CH_3$, is a colourless liquid of sp. gr. 0·7057, which boils at 109° (228°·2 F.). It is obtained by the action of sodium on primary isobutylic iodide, $CH_3.CH(CH_3).CH_2I$.

A *nonane*, C_9H_{20}, which is probably the normal primary paraffin, has been isolated by Thorpe and Young from the mixture of hydrocarbons obtained on decomposing solid paraffin by heat (1164); it boils at 147°—148° (296°·6—298°·4 F.), and has the sp. gr. 7279 at 13°·5 (56°·5 F.)

The *nonane* boiling at 136°—138° (276°·8—280°·4 F.), which, according to Pelouze and Cahours, occurs in petroleum, is undoubtedly an isoparaffin. It has a sp. gr. of 0·741 at 15° (59° F.). Two other nonanes are known, namely, *isobutyl-isoamyl:* $CH_3.CH(CH_3).CH_2.CH_2.CH_2.CH(CH_3).CH_3$, formed by the action of sodium on the mixed isobutylic and isoamylic iodides, and *isobutyl-β-isoamyl:* $CH_3.CH(CH_3) CH_2.CH(CH_3).CH(CH_3).CH_3$, produced in small quantity by treating isopropylic iodide with sodium amalgam (Silva. *Deut. chem. Ges. Ber.* 1872. 984). They are both colourless liquids, the first boiling at 132° (269°·6 F.), the second at about 130° (266° F.).

Normal decane, $C_{10}H_{22}$, boiling at 166°—168° (330°·8—334°·4 F.) has been obtained by Thorpe and Young from the mixture of hydrocarbons from paraffin already referred to.

The *decane* boiling at 158°—162° (316°·4—323°·6 F.), found by Pelouze and Cahours in petroleum, and another compound boiling at 155°—162° (311°—323°·6 F.), which is formed by the action of fuming hydriodic acid on turpentine at 275° (527° F.), are perhaps isomeric paraffins. *Diamyl* or *diisoamyl:* $CH_3.CH(CH_3).CH_2.CH_2.CH_2.CH_2.CH(CH_3).CH_3$, is a colourless oil of density 0·770, which boils at 158° (316°·4 F.). It is prepared in the usual way by the action of sodium on isoamylic iodide. It possesses an ethereal odour and burning taste, and when gently heated with concentrated nitric acid it is violently attacked, yielding, besides succinic acid, a liquid which contains various volatile acids of the acetic series.

The compounds from $C_{12}H_{26}$ to $C_{16}H_{34}$ have been obtained from petroleum, but have, as yet, been but little examined. *Normal dodecane*, $C_{12}H_{26}$, boiling at 202° (395°·6 F.), is formed by the action of sodium on normal hexylic iodide, and also during the electrolysis of potassic œnanthate, $C_6H_{13}.COOK$. *Palmitane*, the normal *heccadecane*, $C_{16}H_{34}$, or $CH_3.(CH_2)_{14}.CH_3$, has been prepared from normal octylic iodide. It crystallizes in white glistening scales, and melts at 21° (69°·8 F.). It boils at 278° (532°·4 F.).

(1164) *Paraffin.*—The higher members of the paraffin series, containing more than 16 atoms of carbon, are solid at the ordinary temperature, and constitute commercial "paraffin," now so largely used in the manufacture of candles; it is not improbable, however, that members of the olefine series are sometimes present in this mixture.

The following account of the production of paraffin on the large scale is from a lecture (Dec. 1872) by Mr. F. Field, F.R.S:—"Although discovered by Reichenbach in 1830, who extracted it from the tar obtained by the dry distillation of beech wood, paraffin long remained a chemical curiosity. It was subsequently obtained from vegetable oil, from animal substances, from pit coal, and from shale, but always in small quantities; and it was not until the year 1847 that it really became an article of commerce. In that year the attention of Mr. James Young was directed by Dr. Lyon Playfair to a dark liquid oozing from cracks in the roof of a coal mine near Alfreton, in Derbyshire, and on distilling this oil the distillate was observed to contain bright crystalline specks, which proved to be paraffin. The manufacture of illuminating oil, and of paraffin from this source, was carried on by Mr. Young until the supply was exhausted. He was thus induced to enter upon a series of experiments which resulted in the discovery that paraffin was obtainable by distillation of all bituminous coals, and in 1850 he secured his celebrated patent for the manufacture of paraffin. The material he employed was known as Torbane-hill mineral, a highly bituminous shale, which gave on distillation about 120 gallons of oil per ton; this has recently become exhausted and now shales, yielding from 15 to 35 gallons of oil per ton, according to quality, are made use of. An idea of the importance to which the manufacture has attained will be formed when it is stated that in Scotland alone there are now 68 oil works, which together consume about 782,000 tons of shale annually, and produce about 21,840,000 gallons of crude oil, which yields in round numbers about 10,000,000 gallons of burning oil, 5000 tons of paraffin, and as by-product about 600 tons of sulphate of ammonia.

"The shale is heated to low redness, usually in large iron retorts; a considerable quantity of inflammable gas is given off, and more or less water passes over together with the oil. The crude oil thus obtained is separated from the water, and submitted to distillation in iron retorts. The first portion which passes over is technically known as spirit or naphtha; the next portion collected, of higher boiling point, is the crude burning oil; this is followed by an oil of a still higher boiling point, used for lubricating machinery; and finally the solid or nearly solid paraffin distils over, whilst a carbonaceous residue remains in the retort. The naphtha and burning oil are purified by successive treatment with strong sulphuric acid and soda solution and subsequent distillation, and are then obtained as colourless, strongly refracting, mobile liquids.

"A variety of processes are employed to remove the oil which still adheres to the crude paraffin, and to render it colourless. In some works it is pressed in powerful presses—at first in the cold and afterwards at a gentle heat, then mixed with naphtha and repressed, this operation being repeated several times; finally, it is dissolved in naphtha, and the solution filtered through animal charcoal; on distilling off the spirit the paraffin is obtained in the form of a white mass. By another process, invented by Mr. Sterry, the separation of the oil from the paraffin is effected by centrifugal force. By a process recently invented by Mr. Fordred, the purification is accomplished entirely without the use of naphtha, and the manufacture thus rendered less dangerous. The crude paraffin is first kneaded in bags by machinery in a warm alkaline liquid; it is then submitted to the action first of sulphuric acid and then of soda solution, and finally it is heated to 110° (230° F.), and a quantity of fullers' earth added, and well stirred up with the molten paraffin; this absorbs all the colouring matter, and renders the paraffin as white as snow."

Messrs. F. Field and A. Smith have since introduced artificially prepared magnesic silicate, as a substitute for fullers' earth.

The mixture of hydrocarbons thus obtained is colourless and beautifully translucent, melting at temperatures varying from 40° to 60° (104° to 140° F.), according to the source from which it was derived. It is insoluble in water, but soluble in boiling alcohol to the extent of about 3·5 per cent. of its weight, separating out in great part on cooling in crystalline plates. It is readily soluble in ether, benzene, oil of turpentine, and carbonic bisulphide, but its solubility decreases very rapidly with the rise in melting point. Cold olive oil dissolves it sparingly, but freely when heated with it. Paraffin is an excellent insulator of electricity. It does not dissolve camphor, naphthalene, or pitch, when fused with them, but may readily be mixed with stearin, spermaceti, bees' wax, and common resin. It burns with a bright smokeless flame, candles made of it being as good as those of the finest wax.

The paraffin isolated by Reichenbach from wood-tar and particularly from beech-tar comes over during the last stages of the distillation when the crude tar is rectified. At ordinary temperatures beech-wood paraffin is a hard crystalline white substance, without either taste or odour, of sp. gr. 0·87, somewhat brittle, and resembling spermaceti both to the touch and in appearance. It fuses at 43°·8 C. (110°·7 F.) to a colourless oily liquid, which remains transparent after solidification, and at a higher heat may be distilled unchanged.

Paraffin is not altered by alkalies, neither is it appreciably acted upon even by the strongest sulphuric acid, unless at very high temperatures. Sealed up in tubes with hydrochloric acid gas, and heated to temperatures varying from 50°—100° (122°—212° F.) it undergoes no change of melting point, and absorbs none of the gas. An aqueous solution of hydrochloric acid is also without effect. When heated or exposed to sunlight in contact with bromine and water it becomes soft at the same time that the bromine disappears; however, all the bromine which enters into the paraffin does so by replacing hydrogen, none combining directly (Gill and Meusel). Chlorine acts similarly. Paraffin is not affected by hypochlorous acid. According to Gill and Meusel (*Chem. Soc. Journ.*, 1868, 466), when paraffin melting at about 60° (140° F.) is boiled with a mixture of potassic dichromate and sulphuric acid, it is gradually oxidized: a number of acids of the acetic series are produced, and amongst others *cerotic acid*, $C_{27}H_{54}O_2$. Dilute nitric acid gives a similar result, but acids of the succinic series, such as succinic and anchoic acid, are also formed. The production of cerotic acid from paraffin by oxidation is of considerable importance, as it indicates the presence in that substance of a hydrocarbon containing at least 27 atoms of carbon.

By heating paraffin for sixty hours at 90° (194° F.) with a mixture of strong nitric and sulphuric acid, Champion (*Compt. rend.*, lxxiv. 1575) obtained a yellow oil to which he gives the formula $C_{26}H_{52}N_2O_{10}$.

According to recent experiments of Pouchet (*Compt. rend.*, lxxix. 320) paraffin, when oxidized by gently heating it with fuming nitric acid, yields, besides lower acids of the acetic series and their nitration products, a new acid which he terms *paraffinic* acid: $C_{24}H_{48}O_2$. It crystallizes from alcohol and ether in grains, or on slow evaporation, in glistening plates, melting at 45°—47°; it is a very unstable body, being easily altered by oxidizing agents, and does not appear to exhibit the properties which characterize the higher acids of the acetic series, although by composition it is a member of that series. Pouchet did not observe the formation of cerotic acid.

Thorpe and Young (*Roy. Soc. Proc.*, 1873, 184) have shown that when paraffin is exposed to a high temperature in a closed vessel it is almost completely resolved, with the evolution of but little gas, into hydrocarbons which remain liquid at the ordinary temperature. This transformation may easily be effected on the small scale. A few grains of ordinary paraffin are sealed up in a piece of strong combustion-tubing bent in the form of the letter V; the tube is securely surrounded by stout wire gauze, and the limb containing the paraffin is gently heated along its entire length in a gas combustion furnace. If the heat is properly regulated, the paraffin distils over rapidly and solidifies in the cold portion of the tube. The gas flames are then turned down, the tube reversed, and the paraffin again distilled. After a very few repetitions of this process, the paraffin acquires the consistence of butter, and the warmth of the hand is sufficient to liquefy it, whilst after about a dozen distillations it remains permanently liquid.

The mixture of hydrocarbons thus obtained, commences to boil at about 18° (64°·4 F.), but the greater portion boils between 200° and 300° (392°—572° F.). Thus 3½ kilograms of solid paraffin melting at 46° (114°·8 F.) gave about 4 litres of liquid hydrocarbons, of which on distillation, 0·3 litres passed over below 100° (212° F.), 1 litre between 100° and 200° (212° and 392° F.), and 2·7 litres at 200°—300° (392°—572° F.); a considerable quantity of solid substance (unaltered paraffin) remaining in the retort.

The paraffin, by this means, is split up into a mixture of lower paraffins and hydrocarbons of the C_nH_{2n} or olefine series. Thus from the fraction below 100°, Thorpe and Young isolated the following bodies:

Paraffins: C_nH_{2n+2}.		Olefines: C_nH_{2n}.	
Pentane	C_5H_{12}	Pentylene	C_5H_{10}
Hexane	C_6H_{14}	Hexylene	C_6H_{12}
Heptane	C_7H_{16}	Heptylene	C_7H_{14}

The fraction 100°—200° (212°—392° F.) yielded:

Paraffins: C_nH_{2n+2}.		Olefines: C_nH_{2n}.	
Hexane	C_6H_{14}	Hexylene	C_6H_{12}
Heptane	C_7H_{16}	Heptylene	C_7H_{14}
Octane	C_8H_{18}	Octylene	C_8H_{16}
Nonane	C_9H_{20}	Nonylene	C_9H_{18}
Decane	$C_{10}H_{22}$	Decylene	$C_{10}H_{20}$
Undecane	$C_{11}H_{24}$	Undecylene	$C_{11}H_{22}$.

The fraction 200°—300° (392°—572° F.) was proved to be a mixture of still higher paraffins and olefines.

The portions of lower boiling-point appear to be mixtures of paraffins and olefines in equal proportions, that is to say they contain equal numbers of molecules of corresponding paraffins and olefines, but the proportion of paraffin to olefine in the several mixtures was observed to become gradually larger as the molecular weight increased. The paraffins obtained belong to the series of so-called 'normal paraffins.'

(1165) *Bitumen, Asphalt, and Petroleum.*—Deposits of these substances are found in various localities, as, for example, at Trinidad, at Zante, and in some parts of the north of Italy, and also on the borders of the Caspian Sea, where petroleum occurs in beds of marl above coal measures. Petroleum is likewise abundant at Rangoon, and in several other localities of the kingdom of Burmah, where the naphtha is obtained from a pale blue clay, soaked with oil, which rests upon roofing slate, beneath which is coal containing much pyrites. The *petroleum* (*petri oleum*, rock oil) from the last-named locality has been made the subject of examination by De la Rue and Hugo Müller (*Proc. Roy. Soc.*, viii. 221). It is obtained by sinking wells about 60 feet deep, in which the liquid is collected as it oozes from the soil. At common temperatures it has the consistence of goose fat; it is lighter than water, and has usually a greenish-brown colour; it has also a slight, peculiar, but not unpleasant odour. It is composed almost entirely of volatile constituents, about 11 per cent. of which come off below 100° (212° F.). The fixed residue does not amount to more than 4 per cent. if it be distilled in a current of superheated steam. About 10 or 11 per cent. of the volatile matters consist of a body which is solid at ordinary temperatures, but fusible at 65° (149° F.) (paraffin). When the liquid portion is agitated with sulphuric acid, some of its constituents enter into combination with the acid, but the greater part remains unaltered by this agent. In the portion which combines with the acid, benzene, toluene, xylene, and cumene have been identified, and there are also several basic substances which have not, as yet, been completely examined. The liquid from which the hydrocarbons of the benzene series have been removed by the action of sulphuric acid, after being rectified, constitutes *rock oil*, or *mineral naphtha*; this liquid requires about eight times its bulk of alcohol for solution, but is soluble in all proportions in ether and in the volatile oils. Hot naphtha dissolves phosphorus and sulphur, but deposits the greater portion of these bodies on cooling. It also dissolves caoutchouc, camphor, and fatty and resinous bodies generally. Warren and Storer (*Memoirs of the American Academy*, 1866, ix. 208) have isolated from it a number of hydrocarbons which they regarded as members of the olefine series, viz.:

	B. P. (Cent.)	Sp. Gr.	
Decylene or Rutylene	about 175°	·823 at 0°	$C_{10}H_{20}$
Endecylene or Margarylene	„ 195°	·839 at 0°	$C_{11}H_{22}$
Dodecylene	„ 215°	·854 at 0°	$C_{12}H_{24}$
Tridecylene	„ 235°	·844 at 0°	$C_{13}H_{26}$

Judging, however, from the boiling-points and specific gravities of these compounds, it is more probable that they are paraffins contaminated with hydrocarbons of the C_nH_{2n-6}, or benzene series. They also found small quantities of naphthalene among the constituents of Rangoon petroleum. Pelouze and Cahours (*Ann. Chim. Phys.* [4], i. 5) have published an account of their researches on American petroleum, and it has since been carefully investigated by Schorlemmer. The oil-wells of Pennsylvania are worked by boring into the oil-bearing strata to a depth of from 50 to 500 feet, and a mixture of oil and water is raised to the surface, usually by pumping; sometimes the oil overflows from the boring. There is one of these wells which yields more than 7000 gallons of petroleum a day.

Four products are furnished for sale from these oils: 1st. A naphtha, used extensively as a solvent instead of oil of turpentine; 2nd. A heavier and less volatile oil, suitable for illuminating purposes; 3rd. A lubricating oil, used for machinery; and 4th. A still heavier oil, used for adulterating vegetable oils.

These oils are furnished by the limestone rocks of the Silurian and Devonian formations.

The bulk of these oils consists of a mixture of various members of the paraffin series, including thirteen different compounds —Tetrane, C_4H_{10}, being the lowest term of the series, and hexadecane or palmitane, $C_{16}H_{34}$, the highest as yet isolated; the most abundant of these compounds is hexane, C_6H_{14}, and the next in amount heptane, C_7H_{16}.

In Canada also vast quantities of petroleum have been obtained, many of the oil-wells yielding 600 gallons of oil per day. According to Sterry Hunt this oil comes from the carboniferous limestone which crops out at Port Erie, and crosses the country to Lake Huron, being in parts overlaid by a thick bed of shale of the Hamilton group.

Asphalt is the term given to solid bitumen. The bitumens differ in the facility with which they are attacked by solvents. Generally they contain but little of any matter soluble in alcohol, but most of them are dissolved in great part by ether, and by oil of turpentine. When distilled they yield substances which resemble the paraffin oils in properties and consistence.

Haloid Derivatives of the Paraffins.

(1166) The action of chlorine converts the paraffins into chlorinated derivatives, one or more atoms of hydrogen being displaced by an equivalent quantity of the halogen. Bromine in most cases attacks them in a similar, although less energetic manner, whilst iodine appears to have no action.

In the preparation of the monochlorinated paraffins, higher substituted derivatives are always formed at the same time, even when the proportions of chlorine and hydrocarbon employed are exactly those required by the equation:

$$C_nH_{2n+2} + Cl_2 = C_nH_{2n+1}Cl + HCl.$$

Thus, when a mixture of equal volumes of chlorine and methane is exposed to diffused daylight, besides monochloromethane, CH_3Cl, more or less dichloromethane, CH_2Cl_2, trichloromethane, $CHCl_3$, and tetrachloromethane, CCl_4, are always formed, according to the conditions of the experiment, whilst a certain quantity of the methane remains unattacked. Schorlemmer, however, has pointed out that in the case of the liquid paraffins, the formation of higher substituted derivatives may be almost entirely avoided by acting on the vapour of the boiling hydrocarbon (*Ann. Chem. Pharm.*, clxi. 263). The monochlorinated paraffin, being less volatile than the hydrocarbon itself, becomes in great part condensed at the moment of formation, and is thus removed from the sphere of action.

(1167) The pure mono-haloid derivatives of the paraffins are most conveniently prepared from the corresponding monohydric alcohols of the $C_nH_{2n+1}.OH$ or ethylic series, by the action of the haloid phosphorus compounds, or haloid acids; thus:

$$3C_nH_{2n+1}.OH + PCl_3 = 3C_nH_{2n+1}Cl + PO_3H_3.$$

$$\underset{\text{Butylic alcohol.}}{3C_4H_9.OH} + PCl_3 = \underset{\substack{\text{Chlorotetrane or}\\ \text{butylic chloride.}}}{3C_4H_9Cl} + PO_3H_3.$$

$$C_nH_{2n+1}.OH + HBr = C_nH_{2n+1}Br + OH_2.$$

$$\underset{\text{Propylic alcohol.}}{C_3H_7.OH} + HBr = \underset{\substack{\text{Bromopropane or}\\ \text{propylic bromide.}}}{C_3H_7Br} + OH_2.$$

$$C_nH_{2n+1}.OH + HI = C_nH_{2n+1}I + OH_2.$$

$$\underset{\text{Hexylic alcohol.}}{C_6H_{13}.OH} + HI = \underset{\substack{\text{Iodohexane or}\\ \text{hexylic iodide.}}}{C_6H_{13}I} + OH_2.$$

Mono-haloid derivatives of the paraffins are also produced by the combination of the haloid acids with the olefines or hydrocarbons of the C_nH_{2n} series :

$$C_nH_{2n} + HBr = C_nH_{2n+1}Br.$$

$$\underset{\text{Propylene.}}{C_3H_6} + HBr = \underset{\text{Bromopropane.}}{C_3H_7Br.}$$

Pure di-derivatives of the paraffins are obtained by combining the olefines with the halogens :

$$C_nH_{2n} + Br_2 = C_nH_{2n}Br_2.$$

The compounds thus produced are in some cases identical with those obtained by the action of the halogens on the isologous paraffins yielding the olefines employed, and in others merely isomeric : thus the dichlorethane, $C_2H_4Cl_2$, formed by the action of chlorine on ethane, is isomeric with the body produced by the combination of chlorine with ethylene, C_2H_4 ; whilst the dichloropropane, $C_3H_6Cl_2$, prepared from propane, is identical with the compound obtained by the direct union of chlorine with propylene, C_3H_6.

The formation of the higher chlorinated derivatives of the paraffins is much facilitated by allowing the action to take place in sunlight, or in presence of iodine or antimonic pentachloride: excepting those derived from methane and ethane, however, they have been but little studied, so that we are not at present aware to what extent it is possible to displace hydrogen by chlorine in the more complex paraffins.

The majority of the haloid derivatives are colourless liquids, insoluble in water ; a few are crystalline solids : they all possess more or less characteristic odours.

According to Schorlemmer's observations (*Ann. Chem. Pharm.*, clxi. 263) the normal primary paraffins, with the exception of methane and ethane, yield two isomeric monochloro-derivatives when acted upon by chlorine, one of which is convertible into a normal primary, the other into a normal secondary alcohol of the $C_nH_{2n+1}.OH$ or ethylic series. We know but little of the behaviour of the hydrocarbons isomeric with the normal primary paraffins when treated with chlorine, although there is reason to suppose that many of them are acted on in a manner similar to the latter: thus Schorlemmer and Grimshaw have shown (*Jour. Chem. Soc.*, 1873, 318) that *ethyl-isoamyl*, a compound isomeric with normal heptane, C_7H_{16}, yields two isomeric monochloro-derivatives under these circumstances.

Our knowledge of the physical properties of the mono-haloid derivatives of the paraffins, such as their boiling-points, and sp. grs. in the liquid state, is extremely imperfect, for excepting in the case of those prepared from the lower terms of the primary alcohols of the ethylic series, the comparison has been made with very small quantities of material, the purity of which, moreover, had often not been satisfactorily established. In the following table (p. 150) the boiling-points (Centigrade) and specific gravities of the better-known mono-haloid paraffin derivatives are given, those classed as α-compounds being either derived from, or convertible into, normal *primary* alcohols of the $C_nH_{2n+1}.OH$ or ethylic series; whilst those classed as β-compounds are correspondingly related to the normal *isoprimary* alcohols of that series.

From an inspection of this table it is evident that the relations between the homologous and isomeric mono-haloid derivatives of the paraffins are of the same nature as those which exist amongst the paraffins themselves. It will be observed that the difference in boiling-point between every two successive homologues diminishes as the series is ascended, also that the primary or α-derivative has a higher boiling-point, and in most (probably in all) instances a higher specific gravity than the isomeric β-derivative; in all cases, moreover, where a greater number of isomeric monohaloid derivatives are known, a similar relation obtains. It is a noteworthy circumstance, and one which clearly illustrates the correlation undoubtedly existing between the physical and chemical properties of compounds, that as the boiling-point and specific gravity of the successive terms in the isomeric series diminish, the compounds become less stable; for example, the members of lowest boiling-point are split up with comparative ease (in some cases even by simply heating to a moderate degree) into the olefine and haloid acid, thus:

$$C_nH_{2n+1}I \quad = \quad C_nH_{2n} \quad + \quad HI;$$

$$\underset{\text{Iodopentane from }\beta\text{-amylene and hydriodic acid.}}{C_5H_{11}I} \quad = \quad \underset{\text{Pentene or amylene.}}{C_5H_{10}} \quad + \quad HI;$$

whilst those of highest boiling-point are far less readily decomposed. Moreover, the haloid derivatives of high boiling-point enter into double decomposition less readily than their isomerides of lower boiling-point, a higher temperature, or more prolonged contact between the substances being required to effect the chemical change.

	α-Compounds.			β-Compounds.		
Formula.	B. P.	Specific Gravity.	Observer.	B. P.	Specific Gravity.	Observer.
	°			°		
CH_3Cl	— 22					
C_2H_5Cl	12·18	·917 at 8°	Linnemann *			
C_3H_7Cl	46·40	·895 at 19°	„			
	46·50	·915 at 0° ·891 at 19°·75	Pierre-Puchot.†			
C_4H_9Cl	77·96	·897 at 14°	Linnemann.	68·5	·879 at 15°	Linnemann.
	78·30	·907 at 0° ·887 at 20°	Lieben.‡	69·0	·805 at 0°	Pierre.
$C_5H_{11}Cl$	117·35	·901 at 0° ·883 at 20°	„	102	·895 at 0°	„
CH_3Br	13					
C_2H_5Br	38·78	1·468 at 13°·5	Linnemann.			
C_3H_7Br	70·82	1·357 at 16°	„			
	70·50	1·353 at 16°	Chapman §			
	72·00	1·349 at 0°	Pierre.			
C_4H_9Br	99·88	1·299 at 20°	Linnemann.	92·33	1·203 at 16°	Linnemann.
	101·00	1·305 at 0° 1·279 at 20°	Lieben.	90·50	1·249 at 0°	Pierre.
$C_5H_{11}Br$	129·46	1·246 at 0° 1·223 at 20°	„	121·00	1·217 at 16°	Chapman.
CH_3I	43·8	2·2 at 0°	Pierre.			
C_2H_5I	72·34	1·944 at 14°·5	Linnemann.			
C_3H_7I	102·18	1·747 at 16°	„			
	102·50	1·734 at 16°	Chapman.			
C_4H_9I	129·82	1·580 at 18°	Linnemann.	120·61	1·608 at 19°·5	Linnemann.
	130·40	1·643 at 0° 1·613 at 20°	Lieben.	122·50	1·634 at 0°	Pierre.
$C_5H_{11}I$	156·16	1·543 at 0° 1·517 at 20°	„	146—147	1·511 at 11°	Frankland.

* Linnemann, *Ann. Chem. Pharm.*, clx. 195; clxi. 15, 175; clxii. 16.

† Pierre and Puchot, *Ann. Chem. Pharm*, clxiii. 253.

‡ Lieben and Rossi, *Ann. Chem. Pharm.*, clviii. 137; *Jour. pr. Chem.* [2], iii. 455.

§ Chapman and Smith, *Jour. Chem. Soc.*, xxii. 193, 198.

The boiling-points given by Linnemann are corrected for the portion of the column of mercury in the thermometer which was not exposed to the vapour of the boiling liquid, and are all referred to the same pressure (760 mm. of mercury at 0°). Lieben and Rossi's original numbers are also corrected for the unexposed mercury column in the thermometer, and the pressure at which the experiment was made is given; in order, therefore, to render their observations comparable with Linnemann's, they have been reduced by his formula to the same pressure of 760 mm. of mercury at 0°.—EDS.

(1168) *Haloid derivatives of Methane.*—The following complete series of haloid derivatives of methane has been obtained:

Monochloromethane or methylic chloride . .	CH_3Cl	CH_3Br	CH_3I
Dichloromethane or methylenic chloride . .	CH_2Cl_2	CH_2Br_2	CH_2I_2
Trichloromethane or chloroform	$CHCl_3$	$CHBr_3$	CHI_3
Tetrachloromethane or carbonic tetrachloride.	CCl_4	CBr_4	CI_4

(1169) MONOCHLOROMETHANE, or *methylic chloride:* $CH_3Cl = 50{\cdot}5$, is formed along with other products when a mixture of equal volumes of methane and chlorine is exposed to diffused daylight; but it is most conveniently prepared in a pure state by passing a current of hydrochloric acid into a boiling solution of zincic chloride in twice its weight of methylic alcohol, $CH_3.OH$, or wood-spirit, when it is given off as a colourless gas (Groves, *Jour. Chem. Soc.*, xxvii. 641). When passed into water cooled below 6° (42°·8 F.), methylic chloride forms a crystalline hydrate (Baeyer).

(1170) DICHLOROMETHANE, or *methylenic chloride:* $CH_2Cl_2 = 85$, is formed together with tri- and tetrachloromethane by acting upon monochloromethane with chlorine in bright sunshine; it may be separated by fractional distillation (Perkin, *Jour. Chem. Soc.*, xxii. 1869, 260). Perkin has also obtained it from trichloromethane or chloroform, $CHCl_3$, by the action of nascent hydrogen; it is, however, most advantageously prepared by treating diiodomethane, CH_2I_2, with chlorine (Butlerow, *Zeits. Chem.*, 1869, 276). It is a colourless mobile liquid, which boils at 40°—42° (104°—107°·6 F.); sp. gr. 1·36 at 0° (32° F.).

(1171) TRICHLOROMETHANE, or *chloroform:* $CHCl_3 = 119{\cdot}5$.—This interesting compound is produced by a variety of reactions:

1. Together with tetrachloromethane, when chlorine is made to act upon methane, chloromethane, or dichloromethane.

2. During the decomposition of the trichloracetates by the alkaline hydrates:

$$\underset{\text{Potassic trichloracetate.}}{CCl_3COOK} + KHO = \underset{\text{Trichloromethane.}}{CCl_3H} + K_2CO_3.$$

3. Also by the action of the alkaline hydrates on trichloracetic aldehyde or chloral:

$$\underset{\text{Chloral.}}{CCl_3COH} + KOH = \underset{\text{Trichloromethane.}}{CCl_3H} + \underset{\text{Potassic formate.}}{HCOOK}.$$

4. It is, however, most economically obtained by acting upon dilute alcohol with chloride of lime (bleaching powder). Wood

spirit, acetone, oil of turpentine, and many essential oils, likewise yield it when treated with chloride of lime. Chloroform is readily procured in a state of purity by the following process:—6 parts of chloride of lime, 24 parts of water, and 1 part of alcohol, are to be mixed in a capacious still, and the temperature raised as rapidly as possible till it reaches 82° (180° F.). The distillation is then to be continued until about one and a half parts have passed over; the product, consisting chiefly of chloroform and water, collects in two layers in the receiver—the chloroform constituting the lower layer. It should be decanted from the aqueous portion, and agitated with sulphuric acid in order to destroy traces of volatile oils which accompany it: by another rectification it is obtained in a state of purity.

Chloroform is a colourless, volatile liquid, of high refracting power and sp. gr. 1·497. It boils at 61° (142° F.). It has a powerful agreeable ethereal odour, and a sweet penetrating taste. Alcohol and ether dissolve it in every proportion, but it is very sparingly soluble in water. Concentrated sulphuric acid has no action upon it, and even potassium does not occasion its decomposition. It is inflamed with difficulty, and burns with a greenish somewhat smoky flame, producing hydrochloric acid as well as carbonic anhydride and water. By admixture with an alcoholic solution of potassic hydrate it is decomposed, potassic chloride and formate being produced:

$$\underset{\text{Chloroform.}}{CHCl_3} + 4KHO = \underset{\text{Potassic formate.}}{HCO.OK} + 2OH_2 + 3KCl.$$

An aqueous solution of potassic hydrate does not produce this change, owing to the sparing solubility of chloroform in water.

The vapour of chloroform possesses the remarkable power of producing complete temporary insensibility to pain in the person who has respired it. It may be readily inhaled for this purpose by placing a small quantity of the liquid upon a sponge or a handkerchief which is to be held before the mouth and nostrils: it is very generally employed for rendering patients insensible to pain during severe surgical operations.

It is of great importance that the chloroform used for this purpose should be quite pure. In some cases, when impure, it has been found to undergo spontaneous decomposition on exposure to a strong light. It ought to communicate no colour to sulphuric acid when agitated with it. The liquid itself should be free from colour, and destitute of any chlorous odour. When a few drops are allowed to evaporate on the hand, no unpleasant odour should be left.

Chloroform freely dissolves sulphur, phosphorus, and iodine. It is also a good solvent for fatty and resinous bodies. No other liquid is so perfect a solvent for caoutchouc, which is left unaltered by it on evaporation.

(1172) TETRACHLOROMETHANE, or *carbonic tetrachloride:* $CCl_4 = 154$.—This substance was obtained by Regnault from wood-spirit and from chloroform, by exposing them in bright sunshine to the action of an excess of chlorine. Kolbe also found that a mixture of the vapour of carbonic bisulphide and dry chlorine, when passed through a red hot porcelain tube yields the same compound mixed with chloride of sulphur: $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$; it is also obtained mixed with chloride of sulphur, on passing chlorine into a mixture of carbonic bisulphide and antimonic chloride, or a warm solution of iodine in the bisulphide, and may be readily prepared in this manner. If the mixture be distilled and the first portions of the distillate agitated with a solution of potassic or sodic hydrate, the chloride of sulphur is decomposed, and the tetrachloride subsides; it may then be decanted and purified by distillation. It is a colourless liquid of sp. gr. 1·599, and boils at 78° (172°·4 F.); it is insoluble in water, but soluble in alcohol and in ether; an alcoholic solution of potassic hydrate decomposes it into potassic chloride and carbonate; $6KHO + CCl_4 = 4KCl + K_2CO_3 + 3OH_2$. If its vapour, diluted with air, be respired it exerts an anæsthetic action on the system. Tetrachloromethane becomes a crystalline solid of pearly lustre, when exposed to a temperature of about −23° (−9° F.). If passed through red-hot tubes it is decomposed into free chlorine and a mixture of *tetrachlorethylene*, C_2Cl_4, and *hexachlorethane* or Faraday's sesquichloride of carbon, C_2Cl_6. By the action of nascent hydrogen, tetrachloromethane may be converted successively into tri-, di-, and monochloromethane, and finally into methane itself.

(1173) MONOBROMOMETHANE, or *methylic bromide:* $CH_3Br = 95$.—This compound is formed by the action of the bromides of phosphorus, or of hydrobromic acid, on methylic alcohol; it is a colourless liquid which boils at 13° (55°·4 F.).

DIBROMOMETHANE, or *methylenic bromide:* $CH_2Br_2 = 174$, is produced on heating monobromomethane with bromine in sealed tubes for 3—4 hours at about 250° (482° F.) (Steiner, *Deut. chem. Ges. Ber.*, vii. 507); and also by the action of bromine on di- and tri-iodomethane. It boils at 80°—82° (176°—179°·6 F.); sp. gr. 2·084 at 11°·5 (52°·7 F.).

TRIBROMOMETHANE, or *bromoform:* $CHBr_3 = 253$.—This compound is obtained on heating bromomethane with the requisite quantity of bromine at

250° (482° F.) (Steiner); also by the decomposition of bromal, C_2HBr_3O, by alkalis; and on distilling alcohol with bromide of lime. It boils at 150° (305°·6 F.), but is at the same time partially decomposed; its sp. gr. is 2·9.

TETRABROMOMETHANE, or *carbonic tetrabromide:* $CBr_4 = 332$.—Carbonic tetrabromide is formed on heating bromoform or carbonic bisulphide with excess of bromine, in the presence of iodine or antimonic bromide, for several hours at 150° (302° F.) in sealed tubes. It is most readily obtained, however, by decomposing bromopicrin, $CBr_3(NO_2)$, by heat. It crystallizes in white lustrous plates, which melt at 91° (195°·8 F.); it boils at 189°·5 (373°·1 F.), but when distilled under the ordinary pressure undergoes slight decomposition. Carbonic tetrabromide has an ethereal odour and sweetish taste; it is very soluble in hot alcohol, ether, and carbonic disulphide. (Bolas and Groves, *Jour. Chem. Soc.*, 1870, xxiii. 161; 1871, xxiv. 773.)

(1174) IODOMETHANE, or *methylic iodide:* $CH_3I = 142$, is best prepared by gradually adding 7 parts of amorphous phosphorus to a mixture of 100 of iodine and 50 of methylic alcohol contained in a retort or flask immersed in cold water and connected with a condenser. The product is distilled, agitated with water, then, after separation from the latter, dried over calcic chloride, and finally rectified. It is a colourless mobile liquid, of peculiar ethereal odour, insoluble in water, boiling at 42° (107°·6 F.), and has a sp. gr. of 2·2 at 0° (32° F.).

DIIODOMETHANE, or *methylenic iodide:* $CH_2I_2 = 268$.—This compound is formed on boiling iodoform with an aqueous solution of potassic hydrate and a little alcohol, and comes over with the aqueous vapour. It is also produced by heating iodoform with hydriodic acid (Lieben): $CHI_3 + HI = CH_2I_2 + I_2$. The best method of preparation, however, is that of Baeyer (*Deut. chem. Ges. Ber.*, v. 1095), who digests the iodoform with aqueous hydriodic acid, adding phosphorus in small pieces from time to time. When pure it is a colourless liquid, which, however, rapidly becomes yellow. It boils at 181° (357°·8 F.). and solidifies at 0° (32° F.) to a colourless crystalline mass which melts at 6° (42°·8 F.); its sp. gr. at 5° (41° F.) is 3·342.

TRIIODOMETHANE, or *Iodoform:* $CHI_3 = 394$.—Iodoform is a product of the action of iodine in presence of potassic or sodic hydrate or carbonate on ethylic alcohol, aldehyde, acetone, and many other substances. According to Lieben, however, who has examined the behaviour of various bodies with iodine and potassic hydrate (*Ann. Chem. Pharm. Sup.*, 7, 281), methylic alcohol does not yield iodoform. To prepare it, 1 pt. of alcohol is added to a solution of 2 pts. crystallized sodic carbonate in 10 pts. water, and the liquid heated to 60° or 80°, (140°—176° F.); 1 pt. of iodine is then added by small portions till it is entirely dissolved, and the liquid has become colourless. Towards the end of the operation the iodoform makes its appearance, and is separated by filtration. The filtrate is then again heated to 60°—80° (140°—176° F.); another portion of sodic carbonate, equal to the former, is dissolved in it; a fresh portion of alcohol is now added, and a current of chlorine is passed into the liquid, which must be continually agitated, so that the iodine which separates may mix well with it. When the process is so conducted that a slight excess of iodine is always present iodoform is produced in abundance. When a considerable quantity has been deposited, the stream of chlorine is interrupted, the liquid is left to decolorize, and the iodoform is filtered off; after which the mother liquor may be again treated with chlorine. Iodoform has a peculiar odour, and crystallizes in pale yellow nacreous scales, which under the microscope are seen to be six-sided plates. It is not perceptibly soluble in water, but dissolves readily in alcohol and ether. It melts at 120° (248° F.), and is decomposed at a higher temperature.

TETRAIODOMETHANE, or *carbonic tetriodide:* $CI_4 = 520$.—Gustavson (*Ann. Chem. Pharm.*, clxxii. 173), has recently obtained this compound by adding tetrachloromethane to aluminic iodide, Al_2I_6, dissolved in carbonic bisulphide. It crystallizes in regular octahedra of a dark red colour, of sp. gr. 4·32 at 20°·2 (68°·4 F.). Boiled with water it yields iodoform, and when heated alone it is decomposed with liberation of iodine.

(1175) *Haloid Derivatives of Ethane.*—All the chloro-derivatives of this hydrocarbon are known, but the corresponding bromine and iodine compounds have been, as yet, but imperfectly examined.

(1176) MONOCHLORETHANE, or *ethylic chloride:* $C_2H_5Cl = 64{\cdot}5$; $CH_3.CH_2Cl$.—Monochlorethane is the first product of the action of chlorine in diffused daylight on ethane (Schorlemmer, *Proc. Roy. Soc.*, xiii. 225; Darling, *Jour. Chem. Soc.*, 1868, xxi. 496); and it is also obtained by saturating ethylic alcohol with hydrochloric acid, and then distilling the product at a gentle heat. The most advantageous method of preparation, however, is to pass a current of gaseous hydrochloric acid into a boiling solution of fused zincic chloride in about twice its weight of alcohol. The vapour of the chloride, after being washed by water, is passed into alcohol, kept cool by surrounding it with cold water. As alcohol at 16° (60°·8 F.) dissolves half its weight of the chloride, this solution may be preserved in an ordinary bottle, and the chloride expelled when required by gently heating it; after being washed with concentrated sulphuric acid it is quite pure. (Groves, *Jour. Chem. Soc.*, 1874, xxvii. 636.) Monochlorethane is readily condensed to a colourless mobile liquid, of a pleasant ethereal odour, which boils at 12°·18 (53°·92 F.). It burns with a brilliant flame edged with green, and when passed through a red-hot tube, it is decomposed into ethylene and hydrochloric acid: $C_2H_5Cl = C_2H_4 + HCl$. It is sparingly soluble in water; the solution gives no precipitate with argentic nitrate. When heated with an alcoholic solution of potassic hydrate in a closed tube at 100° (212° F.), it is converted into ethylic ether: $2C_2H_5.Cl + 2KHO = (C_2H_5)_2O + 2KCl + OH_2$ (Balard); but if the vapour be passed over heated potassic hydrate, ethylene is obtained: $C_2H_5Cl + KHO = C_2H_4 + KCl + OH_2$.

DICHLORETHANE: $C_2H_4Cl_2 = 99$.—Two isomeric dichlorethanes are known: *α-dichlorethane*, or *ethylenic chloride*, obtained by combining ethylene, C_2H_4, with chlorine (*vid.* ethylene); and, *β-dichlorethane*, or *ethylidenic chloride*, produced by acting on monochlorethane with chlorine, and also by treating aldehyde with phosphoric pentachloride:

$$\underset{\text{Aldehyde.}}{CH_3.COH} + PCl_5 = \underset{\text{Ethylidenic chloride.}}{CH_3.CHCl_2} + POCl_3.$$

Both are colourless mobile liquids, of an agreeable ethereal odour. The continued action of chlorine on these dichlorethanes gives rise to isomeric tri- and tetrachlorethanes; these, however, yield the same penta- and hexachlorethane on further treatment with chlorine. The following is a list of the known chlorinated derivatives of ethane, together with their boiling points (Centigrade) and specific gravities (Staedel, *Zeits. Chem.*, 1871, 197, 513):

$CH_3.CH_2Cl$.
Monochlorethane (Ethylic chloride).
B.P. 12°·18.

$CH_2Cl.CH_2Cl$. α-Dichlorethane (Ethylenic chloride). B.P. 84°; S.G. 1·256 at 12°.	$CH_3.CHCl_2$. β-Dichlorethane (Ethylidenic chloride). B.P. 60°; S.G. 1·174 at 17°.
$CH_2Cl.CHCl_2$. α-Trichlorethane. B.P. 115°; S.G. 1·422 at 17°.	$CH_3.CCl_3$. β-Trichlorethane. B.P. 75°; S.G. 1·372 at 0°.
$CHCl_2.CHCl_2$. α-Tetrachlorethane. B.P. 147°; S.G. 1·614 at 0°.	$CH_2Cl.CCl_3$. β-Tetrachlorethane. B.P. 127°·5; S.G. ?

$CHCl_2.CCl_3$.
Pentachlorethane.
B.P. 158°.

$CCl_3.CCl_3$.
Hexachlorethane.
Melts at 226°; B.P. 331°.

(1177) **MONOBROMETHANE**, or *ethylic bromide*: $C_2H_5Br = 109$. —This compound is obtained in a state of great purity by mixing ethylic alcohol with phosphorus bromide: $3C_2H_5.OH + PBr_3 = 3C_2H_5Br + H_3PO_3$; but it is more conveniently prepared by adding slowly 4 parts of bromine to a mixture of 45 parts of ethylic alcohol and 4 of amorphous phosphorus, contained in a retort or flask connected with an inverted condenser, care being taken to keep the mass cool. When the whole of the bromine has been added, the bromethane is distilled off on the water-bath, and agitated, first with a weak alkaline solution, and then with water; it is afterwards separated from the water, and placed in contact with sticks of potassic hydrate, or pieces of calcic chloride, and finally distilled. Bromethane is also produced by the action of hydrobromic acid on ethylic alcohol. It is a colourless, mobile liquid, of ethereal odour, boiling at 41° (105°·8 F).

(1178) **DIBROMETHANE**: $C_2H_4Br_2 = 188$.—Two isomeric dibromethanes corresponding to the two isomeric dichlorethanes are known, viz.—*α-Dibromethane*, or *ethylenic bromide*, boiling at 129° (264°·2 F.), prepared by passing ethylene into bromine (*vid.* ethylene); and *β-dibromethane*, or *ethylidenic bromide*, boiling at 110°—112° (230°—233°·6 F.), formed on heating monobromethane with bromine to 170° (338° F.), or by treating aldehyde with phosphoric pentabromide or trichlorodibromide (*Jour. Chem. Soc.*, 1872, xxv. 233).

A number of the higher brominated ethanes have been obtained from ethylenic bromide (*vid.* haloid derivatives of ethylene).

(1179) IODETHANE, or *ethylic iodide*: $C_2H_5I = 156$.—In order to prepare this compound, 70 parts of ethylic alcohol and 7 parts of amorphous phosphorus are placed in a retort, the bulb of which is immersed in cold water, its neck being connected with an inverted condenser; 100 parts of iodine are then gradually added through the tubulure of the retort, and the mixture agitated after each addition of iodine. When the reaction has terminated, the liquid is distilled by the heat of a water-bath; the distillate should be then washed with weak alkali and water, digested on calcic chloride, and re-distilled. The reaction which occurs during this operation may be thus represented:

$$12C_2H_5.OH + 2P + 5I_2 = 10C_2H_5I + 4OH_2 + 2C_2H_5H_2PO_4.$$

Ethylic alcohol. Ethylic iodide or iodethane. Ethylic dihydric phosphate.

Ethylic iodide is a colourless liquid when freshly prepared, but it soon undergoes a partial decomposition, and becomes brown from the liberation of iodine. It boils at 72°·5 (162°·5 F.), and at 0° (32° F.), has the sp. gr. 1·97. When heated with water to 150° (302° F.) in a sealed tube, it becomes decomposed into ordinary ether and hydriodic acid (Frankland); according to Hofmann, if boiled with water and argentic oxide, alcohol and argentic iodide are produced:

$$2C_2H_5I + Ag_2O = 2C_2H_5.OH + 2AgI;$$

and Wurtz finds that when the anhydrous iodide is heated in a sealed tube with argentic oxide, argentic iodide and ordinary ether are formed with facility:

$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI.$$

If a mixture of equivalent quantities of methylic iodide and ethylic iodide be treated with argentic oxide, methyl-ethyl ether $CH_3.O.C_2H_5$ is produced.

Both the bromide and the iodide of ethyl have been extensively employed for the preparation of substitution-compounds containing ethyl; and it was by decomposing ethylic iodide in a sealed tube by means of zinc, that Frankland succeeded in isolating the hydrocarbon known as diethyl or tetrane.

(1180) IODOCHLORETHANE: $C_2H_4ClI = 190·5$, and IODOBROMETHANE: $C_2H_4BrI = 235$, are produced when ethylene is passed into a solution of iodine chloride, or bromide (Maxwell Simpson, *Proc. Roy. Soc.*, xii. 278; xxii. 51). The former is an oily liquid, boiling at 145° (293° F.). The latter is a solid at the ordinary temperature, which melts at 28° (82°·4 F.), and boils at 162°—167° (323°·6—332°·6 F.); an isomeric body, boiling at 144°—147° (291°·2—296°·6 F.), is formed by exposing bromethylene or vinylic bromide, $CH_2 = CHBr$, to the action of hydriodic acid (Pfaundler, Reboul).

(1181) DIIODETHANE: $C_2H_4I_2 = 272$.—*a-Diiodethane*, or *ethylenic iodide*, $CH_2I.CH_2I$, is produced when ethylene is passed into a pasty mixture of alcohol and iodine. It is a white crystalline substance. *β-Diiodethane* or *ethylidenic iodide*, $CH_3.CHI_2$, is formed by the action of aluminic iodide on β-dichlorethane (Gustavson); it is a liquid boiling at 180° (356° F.). According to Berthelot, acetylene, C_2H_2, combines with hydriodic acid forming both a- and β-diiodethane.

(1182) *Haloid Derivatives of Propane.* MONOCHLOROPROPANE: $C_3H_7Cl = 78$.—Two isomeric chloropropanes are known: namely, the *primary propylic chloride*, or *a-chloropropane*, $CH_3CH_2.CH_2Cl$, which is a product of the action of chlorine on propane (Schorlemmer, *Proc. Roy. Soc.*, xvii. 372), and is also obtained on treating primary propylic alcohol with hydrochloric acid or a chloride of phosphorus; and *secondary*, or *isopropylic chloride*, or *β-chloropropane*, $CH_3.CHCl.CH_3$, prepared by treating isopropylic alcohol with hydrochloric acid or a chloride of phosphorus. The latter is also formed by the action of chlorine on propane.

Propylic chloride boils at 46°·5 (115°·7 F.), whilst isopropylic chloride boils at 39° (102°·2 F.); the sp gr. of the former is ·915 at 0° (32° F.), that of the latter ·874 at 10° (37°·5 F.)

(1183) DICHLOROPROPANE: $C_3H_6Cl_2 = 113$.— Four isomeric dichloropropanes have been obtained, viz.:

		B.P. (Cent.)	Sp. Gr.
a-Dichloropropane . . .	$CH_2Cl.CH_2.CH_2Cl$	117°	1·201 at 15°
β-Dichloropropane or propylenic chloride	$CH_3.CHCl.CH_2Cl$	96°	1·165 at 14°
γ-Dichloropropane or propylidenic chloride	$CH_3.CH_2.CHCl_2$	84°—87°	—
δ-Dichloropropane or methylchloracetol	$CH_3.CCl_2.CH_3$	70°	1·082 at 16°

a-Dichloropropane is formed on heating a-dibromopropane with mercuric chloride (Reboul). *β-Dichloropropane*, or *propylenic chloride*, is obtained by the action of chlorine both on propylic and isopropylic chloride, and by the combination of propylene with chlorine:

$$\underset{\text{Propylic chloride.}}{CH_3.CH_2.CH_2Cl} + Cl_2 = \underset{\text{Propylenic chloride.}}{CH_3.CHCl.CH_2Cl} + HCl.$$

$$\underset{\text{Isopropylic chloride.}}{CH_3.CHCl.CH_3} + Cl_2 = \underset{\text{Propylenic chloride.}}{CH_3.CHCl.CH_2Cl} + HCl.$$

$$\underset{\text{Propylene.}}{CH_3.CH = CH_2} + Cl_2 = \underset{\text{Propylenic chloride.}}{CH_3.CHCl.CH_2Cl.}$$

γ-Dichloropropane, or *propylidenic chloride*, is produced by acting upon propionic aldehyde, $CH_3.CH_2.COH$, with phosphoric pentachloride (Reboul, *Compt. Rend.*, lxxvi. 1270). *δ-Dichloropropane*, or *methylchloracetol*, is obtained together with propylenic chloride by the action of chlorine on isopropylic chloride (Friedel and Silva, *Compt. Rend.*, lxxiii. 1379), and in a pure state, by the action of phosphoric pentachloride on acetone, $CH_3.CO.CH_3$, the oxygen in the latter being displaced by an equivalent quantity of chlorine.

(1184) **TRICHLOROPROPANE**: $C_3H_5Cl_3 = 147·5$.—Three isomeric trichloropropanes are known, viz.:

		B.P. (Cent.)	Sp. Gr.
α-Trichloropropane or trichlorhydrin	$CH_2Cl\ CHCl.CH_2Cl$	155°	1·41 at 0°
β-Trichloropropane	$CH_3.CHCl.CHCl_2$	140°	1·402 at 4°
γ-Trichloropropane	$CH_3.CCl_2.CH_2Cl$	123°	1·350 at 0°

α-Trichloropropane, or *trichlorhydrin*, $CH_2Cl.CHCl.CH_2Cl$, is formed when propylenic chloride is acted upon by chlorine in bright sunshine, or in the presence of iodine (Linnemann, *Ann. Chem. Pharm.*, cxxxvi. 48; cxxxix. 17; Schorlemmer, *Proc. Roy. Soc.*, xviii. 29; Friedel and Silva, *Compt. Rend.*, lxxiv. 805); and also by the union of allylic chloride, C_3H_5Cl, with chlorine (Oppenheim, *Ann. Chem. Pharm.*, cxxxiii. 383). It is most readily prepared, however, by heating dichlorhydrin with phosphoric pentachloride:

$$\underset{\text{Dichlorhydrin.}}{CH_2Cl.CH(OH).CH_2Cl} + PCl_5 = \underset{\alpha\text{-Trichloropropane.}}{CH_2Cl.CHCl.CH_2Cl} + POCl_3 + HCl.$$

β-Trichloropropane is obtained together with the α-compound on heating propylenic chloride, $CH_3.CHCl.CH_2Cl$, with dry iodine chloride; whilst *γ-trichloropropane* is the product of the action of chlorine on methylchloracetol, $CH_3.CCl_2.CH_3$, in sunshine (Friedel and Silva, *Compt. Rend.*, lxxiv. 805).

(1185) **TETRACHLOROPROPANE**: $C_3H_4Cl_4 = 182$.—Three of these are known, viz.:

(1). *Allylenic tetrachloride*, $CH_2Cl,CHCl,CHCl_2$, obtained by Hartenstein, (*Jour. pr. Chem.* [2], vii. 312) by combining allylenic dichloride, $CH_2Cl.CH = CHCl$, from dichlorhydrin, with chlorine. It boils at 171° (339°·8 F.); sp. gr. 1·503 at 17°·5 (63°·5 F.). The tetrachloroglycid obtained by Pfeffer and Fittig (*Ann. Chem. Pharm.*, cxxxv. 357), from dichloroglycid and chlorine, was doubtless a mixture of this body with the isomeric compound, $CH_2Cl.CCl_2.CH_2Cl$, since dichloroglycid is a mixture of the two compounds $CH_2Cl.CCl = CH_2$ and $CH_2Cl.CH = CHCl$ (*vid.* dichloropropylene).

(2). *Dichloracetone chloride*, $CH_3.CCl_2.CHCl_2$, prepared by the action of phosphoric pentachloride on dichloracetone, $CH_3.CO.CHCl_2$. It boils at 153° (307°·4 F.); sp. gr. 1·47 at 13° (55°·4 F.). By the action of chlorine on this body it is converted into a crystalline *pentachloropropane*. (Fittig and Borsche, *Ann. Chem. Pharm.*, cxxxiii. 114.)

(3). A crystalline body, melting at 177°—178° (350°·6—352°·4 F.) has been obtained by Schorlemmer (*Proc. Roy. Soc.*, xviii. 29), by the continued action of chlorine on propane in sunshine.

(1186) **HEXACHLOROPROPANE**: $C_3H_2Cl_6 = 251$.—According to Schorlemmer (*Ibid.*) this is the final product of the action of chlorine on propane in bright sunshine in the presence of iodine. It is a colourless heavy liquid, which boils without decomposition at about 250° (482° F.).

(1187) **BROMOPROPANE**: $C_3H_7Br = 123$.—Propylic and isopropylic bromides are obtained from the corresponding alcohols by treating them with hydrobromic acid, or a bromide of phosphorus. The former boils at 71° (159°·8 F.), sp. gr. 1·35 at 16° (60°·8), the latter at 61° (141°·8 F.), sp. gr. 1·32 at 13° (55°·4 F.).

(1188) **DIBROMOPROPANE**: $C_3H_6Br_2 = 202$.—Three isomeric dibromopropanes are known, viz.:

		B.P. (Cent.)	Sp. Gr.
α-Dibromopropane	$CH_2Br.CH_2.CH_2Br$	162°—163°	2·017 at 0°
β-Dibromopropane or propylenic bromide	$CH_3.CHBr.CH_2Br$	141°·3	1·946 at 16°
δ-Dibromopropane or methyl bromacetol	$CH_3.CBr_2.CH_3$	115°—118°	1·39

a-Dibromopropane is formed together with a small amount of *propylenic bromide* (*vid.* propylene), on heating allylic bromide, $CH_2.CH = CH_2Br$, with a saturated solution of hydrobromic acid to 100° (212° F.) (Geromont, *Deut. chem. Ges. Ber.*, iv. 548; Reboul, *Compt. Rend.*, lxxvi. 1270). The remaining compounds are obtained by methods similar to those employed in the preparation of the analogous chloro-derivatives.

(1189) CHLOROBROMOPROPANE: C_3H_6ClBr = 157·5.—According to Reboul (*Compt. Rend.*, lxxviii. 177), the following five isomeric compounds exist:

		B.P. (Cent.)	Sp. Gr.
I.	$CH_2Br.CH_2.CH_2Cl$	140°—141°	1·63 at 8°
II.	$CH_3.CHBr.CH_2Cl$	about 120°	—
III.	$CH_3.CHCl.CH_2Br$	120°	1·585 at 0°
IV.	$CH_3.CH_2.CHClBr$	about 100°	1·60 at 20° (?)
V.	$CH_3.CClBr.CH_3$	93°—95°	1·474 at 21°

The first of these, together with a relatively very small quantity of the second, is formed on heating allylic chloride, $CH_2 = CH.CH_2Cl$, with hydrobromic acid (Reboul); the third is obtained on heating propylenic bromide, $CH_3.CHBr.CH_2Br$, with a solution of mercuric chloride (Friedel and Silva.) A mixture of the fourth and fifth is obtained on heating crude chloropropane—which is a mixture of the two isomerides, $CH_3.CCl = CH_2$ and $CH_3.CH = CCl_2$, with hydrochloric acid (Reboul). According to Henry (*Deut. chem. Ges Ber.*, iv. 604), the two compounds $CH_3.CHBr.CH_2Cl$ and $CH_3.CHCl.CH_2Br$ are identical in physical properties.

(1190) TRIBROMOPROPANE: $C_3H_5Br_3$. = 281.—*a-Tribromopropane, allylic tribromide*, or *tribromhydrin*, $CH_2Br.CHBr.CH_2Br$, may be obtained by acting upon dibromhydrin $CH_2Br.CH(OH).CH_2Br$, with phosphoric pentabromide, or by combining allylic bromide, $CH_2 = CH.CH_2Br$, with bromine. It crystallizes in white prisms, which melt at 16°—17° (60°·8—62°·6 F.), and boils without decomposition at 219°—221° (426°·2—429°·8 F.). (Wurtz, *Ann. Chem. Pharm.*, civ. 247; Henry, *Deut. chem. Ges. Ber.*, iii. 298.)

An isomeric compound boiling at 195° (383° F.) is obtained by the union of monobromopropylene with bromine (Wurtz, *Ann. Chem. Pharm.*, civ. 246; Linnemann, *Ibid.* cxxxv. 55).

(1191) TETRABROMOPROPANE: $C_3H_4Br_4$ = 360.—A crystalline tetrabromopropane melting at 69° (156°·2 F.) was obtained by Linnemann (*loc. cit.* 65) by heating isopropylic bromide with bromine and water to 110°—150° (230°—302° F.) The production of crystalline tetrabromopropanes has also been observed by Aarland, (*Jour. pr. Chem.* [2] vi. 267), and by Hartenstein (*Ibid.* vii. 317). The liquid tetrabromopropane boiling at 225°—230° (437°—446° F.) obtained by Oppenheim (*Ann. Chem. Pharm.*, cxxxii. 126), from allylene (from bromopropylene) and bromine, is probably identical with Cahour's bromopropylenic bromide. Reboul's tetrabromoglycid is probably a mixture of the compound $CH_2Br.CBr_2.CH_2Br$ with $CH_2Br.CHBr.CHBr_2$.

(1192) CHLOROBROMOPROPANES.—Allylic chloride, C_3H_5Cl, forms with bromine the compound $CH_2Br.CHBr.CH_2Cl$, isomeric with that produced from chloropropylene and bromine, and which has the formula $CH_3.CClBr.CH_2Br$; the former boils at 195° (383° F.) the latter at 170° (338° F.).

(1193) IODOPROPANE, C_3H_7I = 170.—Two isomeric iodopropanes exist, *a-Iodopropane*, or *primary propylic iodide*, $CH_3.CH_2.CH_2I$, is prepared by the action of hydriodic acid on normal propylic alcohol. It boils at 102° (215°·6 F.).

β-Iodopropane, secondary or *isopropylic iodide*, $CH_3.CHI.CH_3$, is formed by the combination of propylene, C_3H_6, with hydriodic acid, and by the action of hydriodic acid on allylic iodide:

$$CH_2{=}CH - CH_2I + 2HI = CH_3 - CHI - CH_3 + I_2;$$

but it is most conveniently obtained by distilling glycerin with an excess of concentrated hydriodic acid solution, allylic iodide being first formed thus:

$$\underset{\text{Glycerin.}}{CH_2(OH).CH(OH).CH_2(OH)} + 3HI = \underset{\text{Allylic iodide.}}{CH_2{=}CH - CH_2I} + I_2 + 3OH_2.$$

It is a mobile colourless liquid of peculiar colour, which boils at 89° (192°·2 F.).

Diiodopropane or *propylenic iodide*, $CH_3.CHI.CH_2I$, is formed by the direct union of propylene with iodine. It is a colourless oil, having a peculiar unpleasant odour, and cannot be distilled without decomposition.

(1194) CHLORIODOPROPANES.—Propylene combines with iodine chloride (Simpson); the chloriodopropane thus prepared is isomeric with that formed by the union of chloropropylene with hydriodic acid (Oppenheim): the former is probably represented by the formula $CH_3.CHCl.CH_2I$, and the latter by the formula $CH_3.CClI.CH_3$.

According to Henry *dichloriodopropane*, $C_3H_5Cl_2I$, is produced by the union of allylic chloride with iodine chloride.

Bromiodopropane, C_3H_6BrI, is formed when propylene is passed into a solution of iodine bromide. It is a colourless oil, which boils at 160°—168° (320°—334°·4 F.), but is at the same time partly decomposed (Simpson).

Chlorobromiodopropane, C_3H_5ClBrI, is produced by the union of allylic bromide with iodine chloride; it is a heavy oily liquid (Henry).

(1195) HALOID DERIVATIVES OF THE TETRANES.—The following monohaloid tetrane derivatives have been obtained by the action of the haloid acids or haloid phosphorus compounds on the isomeric butylic alcohols, $C_4H_9.OH$:

	Normal primary or α-compounds. B.P. (Cent.)	Isoprimary or β-compounds. B.P.	Secondary or γ-compounds. B.P.	Tertiary or δ-compounds. B.P.
Butylic chloride .	78°	68°·5	—	50°—52°
„ bromide .	100°·5	92°·3	—	—
„ iodide .	130°	120°·6	117°—118°	99°

Secondary butylic iodide may also be prepared by the action of hydriodic acid on erythrite, $C_4H_6(OH)_4$, and the tertiary iodide by the direct union of butylene, $CH_2{=}C(CH_3)_2$, and hydriodic acid.

Little is known of the higher chlorinated derivatives of tetrane.

DIBROMOTETRANE, $C_4H_8Br_2$.—Three isomeric dibromotetranes have been described, viz.:

		B.P. (Cent.)
α-Dibromotetrane or α-butylenic bromide	$CH_3.CH_2.CHBr.CH_2Br$ ...	166°
β-Dibromotetrane or β-butylenic bromide	$CH_3.CHBr.CHBr.CH_3$ ...	159°
γ-Dibromotetrane or γ-butylenic bromide	$CH_2.CBr(CH_3).CH_2Br$ ...	149°

α-Dibromotetrane is obtained by heating α-bromotetrane (normal primary butylic bromide) with bromine (Linnemann, *Ann. Chem. Pharm.*, clxi. 200), and is probably identical with the bromide of ethylvinyl (*see* butylene) prepared by Wurtz (*Ann. Chem. Pharm.*, clii. 21). *β-Dibromotetrane* is formed by combining the butylene from secondary butylic alcohol with bromine (Lieben, *Ann. Chem. Pharm.*, cl. 109). *γ-Dibromotetrane* is obtained by heating β-iodotetrane (isoprimary butylic iodide) with bromine (Linnemann, *Ann. Chem. Pharm.*, clxii. 34), and by combining the so-called isobutylene from isoprimary butylic alcohol with bromine.

TRIBROMOTETRANE, $C_4H_7Br_3$.—According to Linnemann (*Ann. Chem. Pharm.*, clxii. 34), this compound is almost the sole product of the action of bromine on β-bromotetrane (isoprimary butylic bromide) at 150° (302° F.); it is a liquid which boils at 214°—218° (417°·2—424°·4 F.). Caventou also obtained a tribromotetrane (bromobutylenic bromide) boiling at 208°—215° (406·4°—419° F.) by combining bromobutylene with bromine. The same observer obtained a *tetrabromotetrane* from dibromobutylene and bromine, in the form of a crystalline solid which decomposes at 200° (392° F.) without previously melting (*Ann. Chem. Pharm.*, cxxvii. 94, 347).

(1196) HALOID DERIVATIVES OF THE PENTANES.—α-MONOCHLOROPENTANE, or normal primary amylic chloride, $CH_3.CH_2.CH_2.CH_2.CH_2Cl$, is formed on heating normal primary amylic alcohol with hydrochloric acid (Lieben and Rossi); it is also a product of the action of chlorine on normal pentane (Schorlemmer). It boils at 106°—107° (222°·8—224°·6 F.); sp. gr. ·901 at 0° (32° F.).

β-MONOCHLOROPENTANE, or isoprimary amylic chloride,

$$CH(CH_3)_2.CH_2.CH_2Cl,$$

is obtained from the optically inactive fermentation amylic alcohol and hydrochloric acid, or a chloride of phosphorus; it boils at 102° (215°·6 F.); sp. gr. ·895 at 0° (32° F.). A third monochloropentane, $C(CH_3)(C_3H_7)HCl$, is formed together with α-chloropentane during the chlorination of normal pentane (Schorlemmer, *Ann. Chem. Pharm.*, clxi. 268).

DICHLOROPENTANE, $C_5H_{10}Cl_2$.—Amylene, C_5H_{10}, from fermentation isoprimary amylic alcohol combines with chlorine to form a dichloropentane or amylenic chloride, boiling at about 145° (293° F.) (Guthrie, *Journ. Chem. Soc.*, xiv. 128). An isomeric compound, $CH_3.CH(CH_3).CH_2.CHCl_2$, is formed by the action of phosphoric pentachloride on valeric aldehyde from fermentation amylic alcohol; it boils at about 130° (266° F.) (*Ann. Chem. Pharm.*, cvi. 262). By the action of chlorine on boiling isoprimary amylic chloride, Buff obtained a dichloropentane boiling at 155°—160° (311°—320° F.) (*Ann. Chem. Pharm.*, cxlviii. 349).

Higher chlorinated derivatives of pentane have been obtained by the action of chlorine on isoprimary amylic chloride and on amylenic chloride (Bauer), but little is known of these compounds. By the action of chlorine in bright sunlight, according to Cahours, the pentane from petroleum is finally converted into the compound $C_5H_3Cl_9$.

(1197) HALOID DERIVATIVES OF THE REMAINING PARAFFINS.—Very few of the haloid derivatives of the remaining hydrocarbons of the C_nH_{2n+2} series have been obtained in a state of purity. By the action of chlorine on the various paraffins which they isolated from American petroleum, Pelouze and Cahours prepared the corresponding monochlorinated paraffins; Schorlemmer's researches (*Ann. Chem. Pharm.*, clxi. 263), however, justify the conclusion that the products they obtained were mixtures of isomeric compounds. A number of the dibromo-derivatives have been prepared by combining the olefines with bromine.

(1198) HEXANE DERIVATIVES.—In addition to the monochlorinated compounds formed by the action of chlorine on normal hexane (Pelouze and Cahours, Schorlemmer), a *monochlorhexane* or *hexylic chloride*,

$$CH_3.CH(CH_3).CH_2.CHCl.CH_3,$$

boiling at about 120° (248° F.), is known, which is prepared from the isoprimary hexylic alcohol from mannite; moreover, tertiary hexylic chlorides have been obtained by the action of phosphorus pentachloride on methyl-diethyl-carbinol, $C(CH_3)(C_2H_5)_2OH$; and propyl-dimethyl-carbinol, $C(C_3H_7)(CH_3)_2OH$; the former boils at 110° (230° F.), the latter at 100° (212° F.), both being partially decomposed, however (Butlerow). By the action of chlorine on the hexane diisopropyl, Schorlemmer obtained a chlorohexane boiling at 124° (255°·2 F.); Silva (*Deut. chem. Ges. Ber.*, vii. 953) finds that an isomeric body boiling at 118° (244°·4 F.) is also produced. The former is probably represented by the formula $CH_3.CH(CH_3).CH(CH_3).CH_2Cl$, the latter by $CH_3.CH(CH_3).CCl(CH_3).CH_3$.

According to Pelouze and Cahours, the final product of the action of chlorine in bright sunlight on petroleum hexane is *hexachlorohexane*, $C_6H_8Cl_6$; this observation has been confirmed by Schorlemmer (*Proc. Roy. Soc.*, xviii. 32).

a-Iodhexane, or *normal primary hexylic iodide*, $CH_3.(CH_2)_4.CH_2I$, prepared from normal primary hexylic alcohol, boils at 179°·5 (355° F.); sp. gr. 1·411 at 17°·5 (63°·5 F.). *Isoprimary hexylic iodide*, from fermentation hexylic alcohol, [?$CH_3.CH(CH_3).CH_2.CH_2.CH_2I$], boils at 172°—175° (341°·6—347° F.). *Normal secondary hexylic iodide*, $C(CH_3)(C_4H_9)HI$, which is obtained by the action of hydriodic acid on the hexahydric alcohol mannite:

$$\underset{\text{Mannite.}}{C_6H_8(OH)_6} + 11HI = \underset{\text{Hexylic iodide.}}{C_6H_{13}I} + 6OH_2 + 5I_2,$$

boils at 167°·5 (333°·5 F.); sp. gr. 1·447 at 0° (32° F.).

Dibromohexane, $CH_3.CH_2.CH_2.CH_2.CHBr.CH_2Br$, formed from hexylene and bromine, boils at 195°—197° (383°—386°·6 F.); sp. gr. 1·605 at 0° (32° F.), 1·580 at 19° (66°·2 F.) (Hecht and Strauss, *Ann. Chem. Pharm.*, clxxii. 62).

(1199) HEPTANE DERIVATIVES.—A number of monochlorheptanes have been obtained by the action of chlorine on the heptanes, and by combining the heptylenes with hydrochloric acid. (Schorlemmer, *Ann. Chem. Pharm.*, clxi. 278; *Journ. Chem. Soc.*, xxvi. 319.) Butlerow has also prepared the compounds $CH_3.C(CH_3)_2.C(CH_3)_2Cl$ and $CH_3.C(CH_3)_2.C(CH_3)_2I$ from the alcohol dimethyl-tertiary-butyl carbinol $CH_3.C(CH_3)_2.C(CH_3)_2.OH$; both are white camphor-like substances (*Deut. chem. Ges. Ber.*, viii. 166).

Dichloroheptane, $C_7H_{14}Cl_2$, is produced by the action of phosphoric pentachloride on heptylic or œnanthylic aldehyde; it boils at 190° (374° F.) (Limpricht, *Ann. Chem. Pharm.*, cii. 80).

(1200) OCTANE DERIVATIVES.—The following mono-derivatives have been prepared by the usual methods from normal primary octylic alcohol, $CH_3.(CH_2)_6.CH_2.OH$ (Zincke, *Ann. Chem. Pharm.*, clii. 1):

	B.P. (Cent.)	Sp. Gr.
Monochloroctane or octylic chloride	180°·5	·880 at 16°
Monobromoctane „ bromide	199°	1·116 at 16°
Moniodoctane „ iodide	221°	1·338 „

The normal secondary octylic alcohol, methyl-hexylcarbinol,

$$C(CH_3)(C_6H_{13})H.OH,$$

yields a chloroctane which boils at 171°—173° (339°·8 – 343°·4 F.) (Neison); the corresponding bromo- and iodo-derivatives decompose partially on distillation.

Butlerow has obtained a tertiary octylic chloride, boiling at about 155° (311° F.), from propyl-diethylcarbinol, $C(C_3H_7)(C_2H_5)_2OH$.

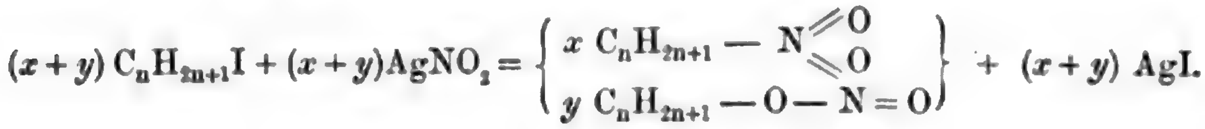
(1201) HEXADECANE DERIVATIVES. — Monochlorhexadecane, or cetylic chloride, prepared by the action of phosphoric pentachloride on cetylic alcohol, is a colourless liquid, distilling above 200° (392° F.) with partial decomposition. The corresponding bromo- and iodo-derivatives are crystalline bodies, melting at 15° (59° F.) and 22° (71°·6 F.) respectively.

NITRO-DERIVATIVES OF THE PARAFFINS.

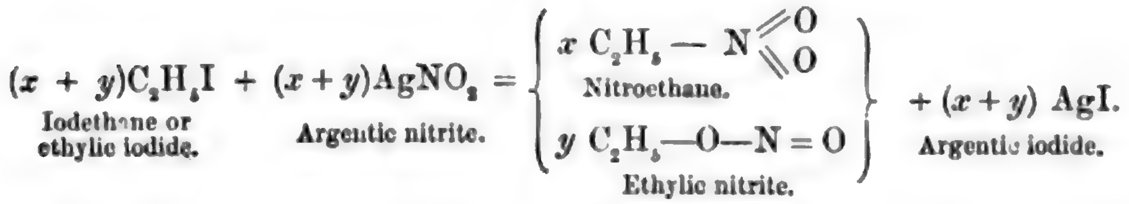
(1202) The following is a list of the known mononitroparaffins:

		B.P. (Cent.)
Nitromethane	$CH_3.NO_2$	101°
Nitroethane	$CH_3.CH_2.NO_2$	111°—113°
Nitropropane (primary) . .	$CH_3.CH_2.CH_2.NO_2$	125°—127°
„ (secondary) .	$CH(CH_3)_2.NO_2$	115°—118°
Nitrotetrane (isoprimary) .	$CH(CH_3)_2.CH_2.NO_2$	137°—140°
„ (tertiary) . .	$C(CH_3)_3.NO_2$	—
Nitropentane (isoprimary) .	$CH(CH_3)_2.CH_2.CH_2.NO_2$	148°—160°

These compounds have all been obtained by V. Meyer and his students* by the action of the corresponding iodoparaffins on argentic nitrite; but, except in the case of the methane derivative, the metameric nitrite (nitrous ether) is always produced at the same time, so that if x be the amount of nitroparaffin, and y the amount of nitrite, which is formed, the reaction may be represented thus:



$$(x+y)\,C_nH_{2n+1}I + (x+y)AgNO_2 = \left\{\begin{array}{l} x\,C_nH_{2n+1} - N\begin{array}{l}\nearrow O\\ \searrow O\end{array} \\ y\,C_nH_{2n+1} - O - N = O \end{array}\right\} + (x+y)\ AgI.$$



$$\underset{\text{Iodethane or ethylic iodide.}}{(x+y)C_2H_5I} + \underset{\text{Argentic nitrite.}}{(x+y)AgNO_2} = \left\{\begin{array}{c} \underset{\text{Nitroethane.}}{x\,C_2H_5 - N\begin{array}{l}\nearrow O\\ \searrow O\end{array}} \\ \underset{\text{Ethylic nitrite.}}{y\,C_2H_5-O-N = O} \end{array}\right\} + \underset{\text{Argentic iodide.}}{(x+y)\ AgI.}$$

Nitromethane has also been obtained by the action of potassic nitrite on monochloracetic acid (Kolbe; Preibisch, *Journ. pr. Chem.* [2] viii. 309). In this case probably the first action consists in the formation of a nitroacetic acid:

$$\underset{\text{Chloracetic acid.}}{CH_2Cl.COOH} + KNO_2 = \underset{\text{Nitroacetic acid.}}{CH_2(NO_2).COOH} + KCl;$$

which is then resolved into nitromethane and carbonic anhydride:

$$\underset{\text{Nitroacetic acid.}}{CH_2(NO_2).COOH} = \underset{\text{Nitromethane.}}{CH_3.NO_2} + CO_2.$$

The mononitroparaffins are colourless, highly refractive mobile liquids of peculiar odour, which are insoluble in water; they distil without decomposition, and their vapours are not explosive. The most characteristic reaction which they exhibit is their conversion into the corresponding amidoparaffins or primary monamines when treated with reducing agents:

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* *Deut. chem. Ges. Ber.*, v. 203. 399, 514, 1029, 1034; vi. 94. 1168, 1492; vii. 425, 670, 709, 712, 786, 790, 916, 962. *Ann. Chem. Pharm.*, clxxi. 1; clxxv. 88.

$$C_nH_{2n+1}.NO_2 + 3H_2 = C_nH_{2n+1}.NH_2 + 2OH_2.$$

$$\underset{\text{Nitroethane.}}{C_2H_5.NO_2} + 3H_2 = \underset{\text{Amidoethane or ethylamine.}}{C_2H_5.NH_2} + 2OH_2.$$

Most of them yield metallic derivatives. Thus, on adding an alcoholic solution of sodic hydrate to nitromethane, to nitroethane, or to the nitropropanes, a white precipitate of the corresponding monosodium derivative is produced; nitroethane, for example, yielding sodium nitroethane:

$$\underset{\text{Nitroethane.}}{C_2H_5.NO_2} + NaOH = \underset{\text{Sodium nitroethane.}}{C_2H_4Na.NO_2} + OH_2.$$

Isoprimary nitrotetrane does not yield a precipitate under these circumstances, although it is soluble in potassic hydrate solution, and may be precipitated unchanged by the addition of an acid; in fact, the tendency to form metallic derivatives diminishes as the series is ascended: for instance, tertiary nitrotetrane and isoprimary nitropentane dissolve in an aqueous solution of potassic hydrate only after long continued agitation, whereas the lower homologues dissolve at once. The aqueous solutions of the sodium derivatives of the nitroparaffins yield characteristic precipitates with the various metallic salts:

	Mercuric chloride.	Mercurous nitrate.	Ferric chloride.	Baric chloride.	Cupric sulphate.	Plumbic acetate.	Argentic nitrate.
Sodium nitromethane.	Pale yellow pp. (very explosive).	Black flocculent pp.	Dark red-brown pp.	No pp.	Leaf-green pp.	White pp.	Yellow pp. which blackens almost immediately.
Sodium nitroethane.	White crystalline pp.	Dirty grey pp.	Blood red coloration.	No pp.	Deep green coloration.	No pp.	White pp. which soon becomes brown.
Sodium nitropropane (primary).	White crystalline pp.	Black flocculent pp.	Blood red coloration.	No pp.	Deep green coloration.	White pp.	White pp. which gradually becomes brown.
Sodium nitropropane (secondary).	White crystalline pp.	Black flocculent pp.	Blood red coloration.	No pp.	Deep green coloration.	No pp.	Pale yellow pp. which rapidly blackens.

When nitromethane is heated with concentrated sulphuric acid, hydroxylamine and carbonic oxide are produced; nitroethane similarly treated, furnishes hydroxylamine and acetic acid, thus:

$$CH_3.C\vert H_2.N\overset{O}{O} + H\vert OH = H_2N.OH + CH_3.COOH.$$

Nitroethane. Hydroxylamine. Acetic acid.

Nitromethane undoubtedly yields in the first place hydroxylamine and *formic acid;* the latter, however, is resolved into carbonic oxide and water by the sulphuric acid. If hydrochloric acid be employed, formic acid is actually obtained; in fact, all the *primary* nitroparaffins yield the corresponding acid of the acetic series and hydroxylamine when heated with hydrochloric acid. When nitroethane is heated with phosphorous acid, the hydroxylamine is reduced, and acetic acid and ammonia are obtained, the phosphorous acid being oxidized to phosphoric acid.

According as the mononitroparaffins are formed from moniodoparaffins derived from primary, secondary, or tertiary alcohols of the $C_nH_{2n+1}.OH$ series they may be classed as *primary, secondary,* or *tertiary* compounds, and distinguished by the following general formulæ:

$$C_nH_{2n+1}.CH_2.NO_2;\quad (C_nH_{2n+1})_2CH.NO_2;\quad (C_nH_{2n+1})_3C.NO_2.$$

Primary nitroparaffin. Secondary nitroparaffin. Tertiary nitroparaffin.

$$CH_3.CH_2.NO_2\qquad (CH_3)_2CH.NO_2\qquad (CH_3)_3C.NO_2.$$

Nitroethane. Secondary nitropropane. Tertiary nitrotetrane.

The three classes are characterized in the following manner:—When a molecule of bromine is added to an aqueous solution of one molecule of the potassium derivative of a primary mononitroparaffin, an oil is obtained which is a mixture of the nitroparaffin with a mono- and a dibromo-derivative; a solution of the potassium derivative of a secondary paraffin thus treated, however, yields as sole product the monobromonitroparaffin. This behaviour is easily explained as follows:—Bromine has no action on the nitroparaffin alone, but when potassium primary nitropropane, for example, is acted upon, a portion of it is converted into bromonitropropane:

$$CH_3.CH_2.CHK.NO_2 + Br_2 = CH_3.CH_2.CHBr.NO_2 + KBr.$$

Potassium nitropropane. Bromonitropropane.

The compound thus produced has a stronger tendency to form metallic derivatives than even the nitroparaffin, and acts upon a portion of the potassium nitropropane still present, forming nitropropane and potassium bromonitropropane:

$$CH_3.CH_2.CHBr.NO_2 + CH_3.CH_2.CHK.NO_2 = CH_3.CH_2.CBrK.NO_2 + CH_3.CH_2.CH_2.NO_2.$$

Bromonitropropane. Potassium nitropropane. Potassium bromonitropropane. Nitropropane.

The potassium bromonitropropane is in turn converted by the bromine into dibromonitropropane, which, however, has no tendency to form metallic derivatives, and is not further acted upon :

$$CH_3.CH_2.CBrK.NO_2 + Br_2 = CH_3.CH_2.CBr_2.NO_2 + KBr.$$

Potassium bromonitropropane. Dibromonitropropane.

On the other hand, potassium secondary nitropropane is converted by the action of the bromine into the secondary bromonitropropane, which does not form metallic derivatives, and therefore is not further acted upon :

$$(CH_3)_2CK.NO_2 + Br_2 = (CH_3)_2CBr.NO_2 + KBr.$$

Potassium secondary nitropane. Bromonitropropane.

It would appear, therefore, that only those nitroparaffins are capable of yielding metallic derivatives in which a part of the hydrogen is united with the carbon atom, which, it may be supposed, is in union with the strongly negative NO_2 group. The fact that the tendency to form metallic derivatives diminishes as the series is ascended, may be explained by supposing that the hydrocarbon group or radicle of the form C_nH_{2n+1}, as it becomes more complex and proportionately richer in carbon, acquires a more negative character, and thus tends more and more to neutralize the negative, or, as it may be termed, acidifying influence of the NO_2 group.

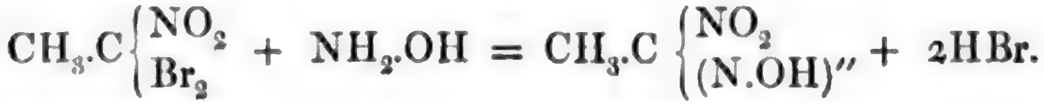
The primary mononitroparaffins are also characterized by their behaviour with nitrous acid, which converts them into so-called *nitrolic acids*. If, for example, nitroethane is dissolved along with potassic nitrite in an aqueous solution of potassic hydrate, and dilute sulphuric acid is added, a magnificent blood-red coloration is at first produced, which disappears as soon as the solution becomes acid ; the ethylnitrolic acid which is formed can then be extracted by ether. The reaction may be represented by the following equation :

$$C_2H_5.NO_2 + NO_2H = C_2H_4N_2O_3 + OH_2.$$

Nitroethane. Ethylnitrolic acid.

Nitrous acid alone, however, has no action on nitroethane, and it appears to be an indispensable condition in the formation of the nitrolic acid, that the nitroparaffin be brought into contact with the nitrous acid at the moment the latter is set free.

Ethylnitrolic acid may also be produced by the action of hydroxylamine on dibromonitroethane, thus :



$$CH_3.C\left\{\begin{matrix}NO_2\\Br_2\end{matrix}\right. + NH_2.OH = CH_3.C\left\{\begin{matrix}NO_2\\(N.OH)''\end{matrix}\right. + 2HBr.$$

Dibromonitroethane. Hydroxylamine. Ethylnitrolic acid.

The acid character of the so-called nitrolic acids is thus shown to be due to their containing the OH group. Their formation from the primary nitroparaffins may be thus represented:

$$\underset{\text{Primary nitroparaffin.}}{C_nH_{2n+1}.CH_2.NO_2} + \underset{\text{Nitrous acid.}}{NO.OH} = \underset{\text{Nitrolic acid.}}{C_nH_{2n+1}.C(N.OH).NO_2} + OH_2.$$

(1203) *Ethylnitrolic acid*, $C_2H_4O_3 = CH_3.C\,(N.OH).NO_2$, crystallizes in large yellow prisms resembling saltpetre crystals; it has an intensely sweet taste and strongly acid reaction. Like the other nitrolic acids, it is readily soluble in all ordinary solvents: its solution in alkalies has a deep-red colour. The metallic derivatives of the nitrolic acids have not as yet been obtained in a state of purity, since they are exceedingly unstable bodies.

Ethylnitrolic acid melts at 81°—83° (177°·8—181°·4 F.), but is at the same time decomposed into acetic acid, nitric peroxide, and nitrogen. By water, and still more readily by concentrated sulphuric acid, it is resolved into acetic acid and nitrous oxide; this decomposition, however, takes place in two stages, thus:

$$\underset{\text{Ethylnitrolic acid.}}{CH_3.C(N.OH).NO_2} + 2OH_2 = \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Nitrous acid.}}{HNO_2} + \underset{\text{Hydroxylamine.}}{NH_2.OH};$$

$$NH_2.OH + HNO_2 = N_2O + 2OH_2.$$

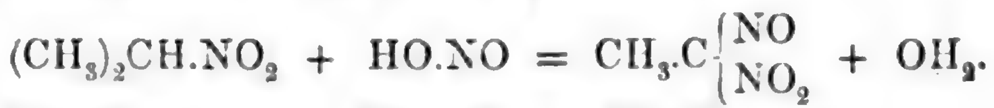
When an aqueous solution is treated with sodium-amalgam, acetic acid, nitrous acid and ammonia are produced. In this case also, hydroxylamine, acetic acid, and nitrous acid are probably formed in the first instance by the action of the water, but the hydroxylamine is simultaneously reduced to ammonia:

$$NH_2.OH + H_2 = NH_3 + OH_2.$$

For we find that when ethylnitrolic acid is reduced by tin and hydrochloric acid, acetic acid and hydroxylamine are obtained:

$$\underset{\text{Ethylnitrolic acid.}}{CH_3.C(N.OH).NO_2} + OH_2 + 2H_2 = \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Hydroxylamine.}}{2NH_2.OH}.$$

(1204) The secondary nitroparaffins behave in an entirely different manner with nitrous acid. For instance, on the addition of dilute sulphuric acid to the solution of secondary nitropropane, $(CH_3)_2CH.NO_2$, in potassic hydrate mixed with potassic nitrite, a magnificent blue colour is developed, and a white crystalline substance separates. This compound, *propylpseudonitrol*, $C_3H_6N_2O_3$, has the same empirical formula as the *propylnitrolic acid* from primary nitropropane, but possesses totally different properties, being insoluble in water and alkalies; it is soluble, however, in warm alcohol or chloroform, forming a magnificent blue solution. It is decomposed when heated to a few degrees above its melting point 76° (168°·8 F.). When oxidized by chromic anhydride, it is converted into *dinitropropane*, $C_3H_6(NO_2)_2$. Most probably propylpseudonitrol is a *nitroso*-nitro-derivative of propane, and its formation from secondary nitropropane would then be represented in the following manner:



$$\underset{\text{Secondary nitropropane.}}{(CH_3)_2CH.NO_2} + \underset{\text{Nitrous acid.}}{HO.NO} = \underset{\text{Nitrosonitropropane.}}{CH_3.C\left\{\begin{matrix}NO\\NO_2\end{matrix}\right.} + OH_2.$$

Higher nitro-derivatives of the Paraffins.

(1205) TRINITROMETHANE, or NITROFORM, $CH(NO_2)_3$.—The ammonium derivative of this body is obtained on boiling the so-called trinitroacetonitrile (1223) with water:

$$\underset{\text{Trinitroacetonitrile.}}{C_2(NO_2)_3N} + 2OH_2 = \underset{\text{Ammonium trinitromethane.}}{C(NO_2)_3(NH_4)} + CO_2.$$

The product is then shaken with sulphuric acid and the nitroform, which floats as an oil on the surface of the acid, is separated. Below 15° (59° F.). nitroform is a colourless crystalline solid, which is moderately soluble in water. It cannot be distilled, and when rapidly heated explodes with violence. It has marked acid properties, and yields a variety of metallic derivatives, most of which are crystalline.

(1206) TETRANITROMETHANE, $C(NO_2)_4$, is prepared by heating nitroform with fuming nitric acid and sulphuric acid to 100° (212° F.). It is liquid at the ordinary temperature, but solidifies at 13° (55°·4 F.); it is insoluble in water. Tetranitromethane is said to distil without decomposition at 126° (258°·8 F.) (Schisckoff, *Ann. Chem. Pharm.*, ciii. 364 and cxix. 247).

(1207) DINITROPROPANE, $C_3H_6(NO_2)_2 = CH_3.C(NO_2)_2.CH_3$, which is formed by oxidizing nitrosonitropropane, is a white crystalline substance closely resembling camphor in appearance. It melts at 53° (127°4 F.), and boils at 185°·5 (366° F.) without decomposition. It is scarcely soluble in water or alkalies, but dissolves easily in alcohol and ether. It volatilizes with the greatest readiness in a current of steam, and sublimes even at the ordinary temperature. By the action of tin and hydrochloric acid, it is converted into *acetone* and hydroxylamine:

$$\underset{\text{Dinitropropane.}}{CH_3.C(NO_2)_2.CH_3} + 4H_2 = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + \underset{\text{Hydroxylamine.}}{2NH_2.OH} + OH_2.$$

(1208) TRINITROPROPANE, $C_3H_5(NO_2)_3 = CH_2(NO_2).CH(NO_2).CH_2(NO_2)$. is formed by the action of *a*-tribromopropane or allylic tribromide on argentic nitrite. (Brackebusch, *Deut. chem. Ges. Ber.*, vi. 289.) It boils at 190°—200° (376°—392° F.). By the action of an alcoholic solution of potassic hydrate it is converted into a tripotassium derivative, $C_3H_2K_3(NO_2)_3$, and when reduced by iron and acetic acid yields triamidopropane or glyceryl-triamine, $C_3H_5(NH_2)_3$.

Haloid nitro-derivatives of the Paraffins.

(1209) The following have been obtained:

		B.P. (Cent.)
Chloronitromethane	CH_2ClNO_2	122°—123°
Trichloronitromethane or chloropicrin . .	CCl_3NO_2	112°
Dichlorodinitromethane (Marignac's oil ?) .	$CCl_2(NO_2)_2$	—
Bromonitromethane	CH_2BrNO_2	143°—144°
Dibromonitromethane	$CHBr_2NO_2$	155°—160°
Tribromonitromethane or bromopicrin . .	CBr_3NO_2	—
Bromotrinitromethane or bromonitroform .	$CBr(NO_2)_3$	—
Bromonitroethane	$CH_3.CHBrNO_2$	145°—148°
Dibromonitroethane	$CH_3.CBr_2NO_2$	162°—164°
Trichlorodibromonitroethane	$CCl_3Br_2NO_2$	—
Trichlorodinitroethane	$C_2Cl_3(NO_2)_3$	—
Bromonitropropane (primary)	$CH_3.CH_2.CHBrNO_2$	155°—165°
Dibromonitropropane „	$CH_3.CH_2.CBr_2NO_2$	184°—186°
Bromonitropropane (secondary)	$(CH_3)_2CBrNO_2$	148°—150°
Dibromonitrotetrane (isoprimary) . . .	$CH(CH_3)_2.CBr_2NO_2$	180°—185°.

(1210) **Chloronitromethane**, CH_2ClNO_2.—Nitromethane is not attacked by chlorine even in the sunshine, but by the action of chlorine on sodium nitromethane chloronitromethane is readily produced (*Deut. chem. Ges. Ber.*, viii. 608). It is a colourless liquid, which possesses a very pungent irritating odour.

(1211) **Trichloronitromethane**, or *chloropicrin*, CNO_2Cl_3.—This body is produced whenever nitro-compounds are distilled with bleaching powder and water, and is also formed when trichloromethane or chloroform, $CHCl_3$, is heated with concentrated nitric acid to 100° (212° F.) (Mills, *Journ. Chem. Soc.*, xxiv. 641). It is best prepared by distilling trinitrophenol or picric acid (1 part) with bleaching powder (10 parts), and water (50 parts); in fact, it was first obtained in this way by Stenhouse, and was from this circumstance called chloropicrin. Trichloronitromethane is a transparent, colourless, highly refractive liquid, of sp. gr. 1·66; it has a peculiar pungent odour, and attacks the nose and eyes most violently. It is insoluble in water. When reduced with iron filings and acetic acid it is converted into amidomethane or methylamine:

$$CCl_3.NO_2 + 6H_2 = CH_3.NH_2 + 2OH_2 + 3HCl;$$

but when heated with hydriodic acid solution (sp. gr. 1·58), it is decomposed in the following manner (Mills):

$$CCl_3NO_2 + 6HI = CO_2 + NH_4Cl + 2HCl + 3I_2.$$

By heating trichloronitromethane with a solution of potassic cyanide, Bassett (*Journ. Chem. Soc.*, xix. 352) obtained a substance which he regards as *dichlorocyanonitromethane*, $CCl_2(CN)NO_2$.

(1212) **Dichlorodinitromethane**, $CCl_2(NO_2)_2$.—When the mixture of chlorinated naphthalenes, formed by passing chlorine into naphthalene until a buttery mass is obtained, is heated with nitric acid, a substance is produced known as Marignac's oil; it is probably dichlorodinitromethane. It closely resembles chloropicrin, but cannot be distilled without undergoing decomposition. Hydriodic acid acts upon it in the following manner (Mills):

$$C(NO_2)_2Cl_2 + 7HI = NH_3 + NO + OH_2 + 2HCl + CO_2 + 7I.$$

(1213) **Bromotrinitromethane**, $CBr(NO_2)_3$, is produced by the action of bromine on trinitromethane or its mercury derivative. It is a liquid, but solidifies at 12° (53°·6 F.) to a crystalline solid; it is decomposed on distillation.

(1214) **Trichlorodibromonitroethane**, $C_2Cl_3Br_2(NO_2)$; **Trichlorotrinitroethane**, $C_2Cl_3(NO_2)_3$.—According to Hoch (*Journ. pr. Chem.* [2] vi. 95), when tetrachlorethylene, C_2Cl_4, is acted upon by a mixture of concentrated nitric and sulphuric acids, a nitrotrichlorethylene, CCl_3NO_2 is produced; by heating with bromine and liquid nitric peroxide respectively, this is converted into the compounds $Cl_3Br_2NO_2$, and $C_2Cl_3(NO_2)_3$.

(1215) The remaining nitrobromoparaffins are obtained by the action of bromine on the nitroparaffins in the manner already indicated. *Tribromonitromethane* is most readily prepared, however, by distilling trinitrophenol with bromide of lime:—4 parts of lime are slaked with 50 of water, and when the mixture is quite cold, 6 parts of bromine are gradually added with constant agitation, great care being taken to prevent any rise of temperature; 1 part of trinitrophenol is then added, and the mixture rapidly distilled from a metal vessel, such as a tin oil-can (Bolas and Groves, *Journ. Chem. Soc.*, 1870, 153).

CYANO-DERIVATIVES OF THE PARAFFINS.

(1216) When bromethane or iodethane is heated with *potassic cyanide*, or when a dry mixture of potassic cyanide[*] and potassic ethylic sulphate is submitted to distillation, the product consists mainly of a *cyanethane*, or *ethylic cyanide*, which yields propionic acid and ammonia when heated with water, in the presence either of an acid or of an alkali; thus:

$$\underset{\text{Bromethane.}}{C_2H_5Br} + KCN = \underset{\text{Cyanethane.}}{C_2H_5.CN} + KBr.$$

$$\underset{\text{Potassic ethylic sulphate.}}{C_2H_5.KSO_4} + KCN = \underset{\text{Cyanethane.}}{C_2H_5.CN} + K_2SO_4.$$

$$\underset{\text{Cyanethane.}}{C_2H_5.CN} + 2OH_2 = \underset{\text{Propionic acid.}}{C_2H_5.COOH} + NH_3.$$

Gautier has shown, however, that if iodethane be heated with *argentic cyanide*, and the product distilled with a potassic cyanide solution, an *isocyanethane*, or *isoethylic cyanide*, is produced, which furnishes formic acid and ethylamine when decomposed with water in the presence of an acid:

$$C_2H_5I + 2AgCN = C_2H_5(CN).AgCN + AgI;$$

$$C_2H_5(CN).AgCN + KCN = C_2H_5.CN + AgCN.KCN.$$

$$\underset{\text{Isocyanethane.}}{C_2H_5.CN} + 2OH_2 = \underset{\text{Ethylamine.}}{C_2H_5.NH_2} + \underset{\text{Formic acid.}}{H.COOH.}$$

In both cases the two cyanethanes are produced,[†] but in the former the product consists mainly of cyanethane, whilst in the latter it consists almost entirely of isocyanethane. Cyanethane is obtained in a state of purity when propionamide is distilled with phosphoric anhydride or phosphoric pentasulphide:

$$\underset{\text{Propionamide.}}{C_2H_5.CO.NH_2} + \underset{\text{Phosphoric anhydride.}}{P_2O_5} = \underset{\text{Cyanethane.}}{C_2H_5.CN} + \underset{\text{Metaphosphoric acid.}}{2HPO_3.}$$

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[*] Potassic ferrocyanide may be advantageously employed instead of potassic cyanide.

[†] The behaviour of other cyanides with the monohaloid paraffins has not hitherto been sufficiently studied: the proportion in which the two cyano-derivatives are produced appears, however, to vary both with the nature of the reacting substances and the conditions of experiment.

On account of its formation in this way, cyanethane is often termed *propionitrile*,* since it may be regarded as a derivative of ammonia, in which the 3 atoms of hydrogen have been displaced by the triad radicle $(\mathrm{C_2H_5.C^{iv}})'''$.

A method has been discovered by Hofmann which yields isocyanethane exclusively. When ammonia acts upon trichloromethane in presence of potassic hydrate, hydric cyanide is formed, thus :

$$\mathrm{HCCl_3 + NH_3 + 3KHO = HCN + 3KCl + 3OH_2}.$$

If, however, the primary monamine, ethylamine, be substituted for ammonia, isoethylic cyanide or isocyanethane is produced :

$$\mathrm{CHCl_3} + \underset{\text{Ethylamine.}}{\mathrm{C_2H_5NH_2}} + \mathrm{3KHO} = \underset{\text{Isocyanethane.}}{\mathrm{C_2H_5.NC}} + \mathrm{3KCl + 3OH_2}.$$

On account of the relation which it bears to ethylamine, isocyanethane is also termed *ethylcarbamine.*

Judging from the manner in which the two cyanethanes are formed and their behaviour when treated with various reagents, they may be represented by the formula :

$$\underset{\text{Cyanethane or Propionitrile.}}{\mathrm{C^{iv}}\left\{\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{N'''}\end{matrix}\right. \text{ or } \mathrm{C_2H_5-C{\equiv}N}}\,; \quad \underset{\text{Isocyanethane or Ethylcarbamine.}}{\mathrm{N'''}\left\{\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C''}\end{matrix}\right. \text{ or } \mathrm{C_2H_5-N{=}C}}.$$

All the methods of preparing the two cyanethanes which have been mentioned may be generalized, and thus a series of compounds may be produced bearing the same relations to the paraffin methane and its homologues, that the cyanethanes bear to ethane.

(1217) The following is a list of the known monocyanoparaffins:

Cyanoparaffins or Nitriles : $\mathrm{C_nH_{2n+1}-C{\equiv}N}$.

		B. P. (Cent.)	Sp. Gr.
Cyanomethane or acetonitrile	$\mathrm{CH_3.CN}$	81°—82°	·79
Cyanethane or propionitrile	$\mathrm{CH_3.CH_2.CN}$	96°—97°	
Cyanopropane (primary) or butyronitrile	$\mathrm{CH_3.CH_2.CH_2.CN}$	115°—117°	
Cyanopropane (secondary) or isobutyronitrile	$\mathrm{CH(CH_3)_2.CN}$	107°—108°	
Cyanotetrane (primary) or valeronitrile	$\mathrm{CH_3.CH_2.CH_2.CH_2.CN}$	141°	·816 at 0°
Cyanotetrane (isoprimary) or isovaleronitrile	$\mathrm{CH(CH_3)_2.CH_2.CN}$	126°—128°	·822 at 0°

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* The tertiary monamines of the form N R''' are commonly termed *nitrile* bases.

		B. P. (Cent.)	Sp. Gr.
Cyanotetrane (tertiary) or trimethacetonitrile . . .	$C(CH_3)_3.CN$	about 103° (?)	
Cyanopentane (isoprimary) or isocapronitrile . . .	$CH(CH_3)_2.CH_2.CH_2CN$	146°	
Cyanopentane (tertiary) or dimethethacetonitrile . .	$C(CH_3)_2C_2H_5CN$	about 130°	
Cyanoheptane (? primary) or caprylonitrile	$CH_3.(CH_2)_5.CH_2.CN$	194°—196°	
Cyanoctane (normal secondary) or pelargonitrile .	$C(CH_3)(C_6H_{13})H.CN$	206°	
Cyanohexadecane or margaronitrile	$C_{16}H_{33}.CN$		

Isocyanoparaffins or Carbamines : $C_nH_{2n+1}-N=C$.

Isocyanomethane or methylcarbamine	$CH_3.NC$	58°—59°	·755 at 14°
Isocyanethane or ethylcarbamine	$CH_3.CH_2.NC$	78°—79°	·758 at 4°
Isocyanopropane (primary) or propylcarbamine	$CH_3.CH_2.CH_2.NC$	95°—100°	
Isocyanopropane (secondary) or isopropylcarbamine . . .	$CH(CH_3)_2.NC$	87°	·759 at 0°
Isocyanotetrane (isoprimary) or isobutylcarbamine	$CH(CH_3)_2.CH_2.NC$	114°—117°	·783 at 0°
Isocyanopentane (isoprimary) or isoamylcarbamine	$CH(CH_3)_2.CH_2.CH_2.NC$	137°	

(1218) *Properties of the Cyanoparaffins or Nitriles.*—The nitriles, it will be observed, in all cases possess a higher boiling point than the corresponding carbamines. They are mobile, colourless liquids of peculiar but not unpleasant odour, and do not appear to be poisonous; the lower terms of the series dissolve easily in water, but the solubility diminishes as they increase in complexity. They combine slowly with hydrochloric acid, and somewhat more readily with hydrobromic and hydriodic acids; thus cyanethane forms with hydrochloric acid the compound $C_3H_5N.HCl$, and with hydrobromic acid the compound $C_3H_5N.2HBr$. They do not unite, however, with the oxacids, such as sulphuric acid, neither do they combine with the moniodoparaffins. They are not affected by argentic or mercuric oxides. The nitriles unite with many chlorides; cyanethane, for example, forming the compounds:

$$C_3H_5N.BCl_3\,;\; C_3H_5N.AuCl_3\,;\; C_3H_5N.SbCl_3\,;\; (C_3H_5N)_2.PtCl_4\,;$$
$$(C_3H_5N)_2.SiCl_4\,;\; C_3H_5N.COCl_2.$$

The cyanoparaffins or nitriles are decomposed when heated with water, and ultimately converted into ammonia and an acid of the acetic series with the same number of atoms of carbon as the nitrile, these of course combine to form the ammonic salt: this change is greatly accelerated by the addition of an alkali, or an acid, such as sulphuric or hydrochloric acid. The first product of the action of water is the corresponding *acid amide:*

$$\underset{\text{Cyanoparaffin.}}{C_nH_{2n+1}.CN} + OH_2 = \underset{\text{Acid amide.}}{C_nH_{2n+1}.CONH_2}.$$

$$\underset{\text{Cyanomethane.}}{CH_3CN} + OH_2 = \underset{\text{Acetamide.}}{CH_3CONH_2}.$$

By the continued action of water the amide is converted into the ammonic salt of the corresponding acid of the acetic series:

$$\underset{\text{Acid amide.}}{C_nH_{2n+1}.CONH_2} + OH_2 = \underset{\text{Ammonic salt of acid.}}{C_nH_{2n+1}.COONH_4}.$$

$$\underset{\text{Propionamide.}}{C_2H_5.CONH_2} + OH_2 = \underset{\text{Ammonic propionate.}}{C_2H_5.COONH_4}.$$

If the action of water take place in presence of an alkali, free ammonia and the alkaline salt of the acid of the acetic series are obtained; in the presence of an acid, on the other hand, the products are the free acid of the acetic series and the ammonic salt of the acid employed.

The cyanoparaffins are converted by the action of nascent hydrogen into the monamidoparaffins, or primary monamines containing the same number of atoms of carbon:

$$C_nH_{2n+1}.CN + 2H_2 = C_nH_{2n+1}.CH_2.NH_2.$$

$$\underset{\text{Cyanomethane.}}{CH_3.CN} + 2H_2 = \underset{\text{Amidoethane or Ethylamine.}}{CH_3.CH_2.NH_2}.$$

These nitriles are readily attacked by sodium and potassium, and are in part decomposed, a metallic cyanide being formed and gas evolved; at the same time a portion undergoes polymerization. Cyanomethane, CH_3CN, may in this way be converted into *cyanmethine*, $C_6H_9N_3$ (Baeyer, *Deut. chem. Ges. Ber.*, ii. 319), and cyanethane, C_2H_5CN, into *cyanethine*, $C_9H_{15}N_3$ (Frankland and Kolbe, *Ann. Chem. Pharm.*, lxv. 288). Both are crystalline compounds, soluble in water; the former melts at 180°—181° (356°—357°·8 F.), the latter at 190° (374° F.). They may be boiled and even melted with potassic hydrate without suffering alteration. They form a series of well-crystallized salts with acids, such as cyanmethane hydrochloride, $C_6H_{10}N_3Cl$; cyanmethine nitrate, $C_6H_{10}N_3NO_3$; cyanethine nitrate, $C_9H_{16}N_3NO_3$; and cyanmethine sulphate, $C_{12}H_{20}N_6SO_4$.

(1219) *Properties of the Isocyanides or Carbamines.*—They are colourless liquids, which possess most nauseous odours, and exert highly deleterious effects, almost immediately producing nausea, vertigo, headache, and depression. The lower terms are soluble in water, but the solubility diminishes as the series is ascended. They combine very readily with the haloid acids and oxacids, much heat being evolved in the act of combination; they also unite with the iodoparaffins at ordinary temperatures. The isocyanoparaffins or carbamines are oxidized with very great readiness by mercuric and argentic oxides, and converted into the corresponding isocyanates or carbimides, thus:

$$C_2H_5NC + HgO = C_2H_5NCO + Hg.$$

Isocyanethane or ethylcarbamine. Ethylic cyanate or ethylcarbimide.

Various secondary products, however, are usually formed at the same time, owing to the violence of the action.

They are only slowly decomposed by pure water, or by an alkaline solution, but are very rapidly changed when acted upon by an aqueous solution of an acid, such as sulphuric or hydrochloric acid. They are first converted into the substituted amide of formic acid:

$$CN.C_nH_{2n+1} + OH_2 = HCO.NHC_nH_{2n+1};$$

$$CN.CH_3 + OH_2 = HCO.NHCH_3;$$

Isocyanomethane or methylcarbamine. Methylformamide.

and finally into formic acid, and the amidoparaffin or primary monamine containing one atom of carbon less than the carbamine:

$$HCO.NHC_nH_{2n+1} + OH_2 = HCOOH + HN_2C_nH_{2n+1},$$

$$HCO.NHCH_3 + OH_2 = HCOOH + NH_2CH_3.$$

Methylformamide. Formic acid. Methylamine.

The carbamines undergo decomposition when heated in closed vessels above their boiling points, but the nature of the products has not, as yet, been satisfactorily ascertained; a portion of the carbamine appears, however, to be converted into the corresponding nitrile.

(1220) *Higher cyano-derivatives of the paraffins.*—The number of these is at present extremely limited. *Tricyanomethane* or *cyanoform*, $CH(CN)_3$, is said to be produced by heating trichloromethane with potassic cyanide (Fairley), or triiodomethane with mercuric cyanide (Pfankuch); in the later case, it is obtained in combination with mercuric iodide as $2CH(CN)_3.3HgI_2$, and can only be separated from it with difficulty.

Dicyanethane, ethylenic cyanide or succinonitrile, $C_2H_4(CN)_2$, *Dicyanopropane* or propylenic dicyanide, $C_3H_6(CN)_2$, and *Tricyanopropane* or allylic tricyanide, $C_3H_5(CN)_3$, have been obtained respectively by the action of α-dibromethane or ethylenic bromide, β-dibromopropane or propylenic bromide, and α-tribromopropane or tribromhydrin on potassic cyanide. All these bodies belong to the class of nitriles.

Haloid Cyano-derivatives of the Paraffins.

(1221) By distilling monochlor-, dichlor-, and trichloracetamide respectively with phosphoric anhydride, the following chlorinated derivatives of cyanomethane or acetonitrile have been obtained (Bisschopink, *Deut. chem. Ges. Ber.*, vi. 731):

		B.P. (Cent.)	Sp. Gr.
Chlorocyanomethane or chloracetonitrile . .	CH_2ClCN	123°—124°	1·204 at 11°·2
Dichlorocyanomethane or dichloracetonitrile .	$CHCl_2CN$	112°—113°	1·374 „ 11°·4
Trichlorocyanomethane or trichloracetonitrile .	CCl_3CN	83°—84°	1·439 „ 12°·2

This series of derivatives affords a very remarkable instance of a depression of boiling-point, resulting from the introduction of chlorine in place of hydrogen.

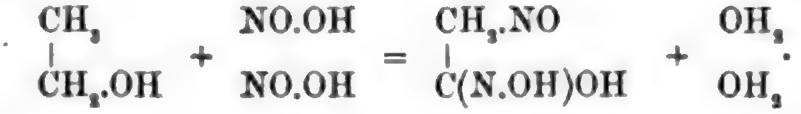
Cyanomethane and cyanethane are converted by heating with bromine into the hydrobromides of monobrominated derivatives: $CH_2BrCN.HBr$ and $C_2H_4BrCN.HBr$. The action of chlorine on cyanethane produces *α-dichlorocyanethane*, $C_2H_3Cl_2CN$.

(1222) *Constitution of the Fulminates.*—When mercuric fulminate (1150) is distilled with bleaching powder solution, trichloronitromethane or chloropicrin is produced, and when it is submitted to the action of chlorine, it also yields trichloronitromethane together with cyanogen chloride and mercuric chloride. These reactions led Kekulé to the conclusion that the fulminates contain the nitro- or NO_2 group, and the cyano- or CN group, and he therefore proposed for the hypothetical fulminic acid the formula $CH_2.NO_2.CN$, which is that of a nitrocyanomethane or nitroacetonitrile, representing the action of chlorine on the mercury derivative by the equation:

$$\underset{\text{Mercuric fulminate.}}{CHg.NO_2.CN} + 3Cl_2 = \underset{\text{Trichloro-nitromethane.}}{CCl_3.NO_2} + \underset{\text{Cyanogen chloride.}}{CNCl} + HgCl_2.$$

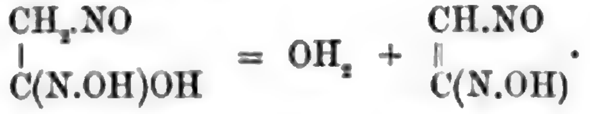
This view of the constitution of the fulminates appears to have been hitherto almost universally adopted; recent additions to our knowledge tend, however, to modify it. Thus Meyer's researches on the nitroparaffins have shown that the introduction of the NO_2 group in place of hydrogen in a paraffin renders only a *single atom* of hydrogen displaceable by metals, whereas *two atoms* of hydrogen in fulminic acid may be displaced; the cyanoparaffins, we know, have no tendency to form metallic derivatives. The formula $CH_2.NO_2.CN$ would indicate, moreover, that the two atoms of hydrogen in fulminic acid are of equal value, but this is not the case; for on heating mercuric or argentic fulminate with potassic hydrate, only half the mercury or silver can be displaced by potassium. Both the cyanoparaffins and the nitroparaffins are compounds of very considerable stability, and it therefore appears likely that a nitrocyanoparaffin would also be a fairly stable substance; but fulminic acid is so unstable that it cannot be isolated. An argument of far greater weight, however, is derived from the consideration of the circumstance that the fulminates are produced by the action of *nitrous acid* on ethylic alcohol in presence of a salt of mercury or silver. Meyer's researches have shown that the action of nitrous acid on the nitroparaffins leads to the displacement of hydrogen either by the NO or *nitroso*-group, or the

N.OH group; in no case does nitrous acid produce nitro-derivatives. The following may therefore be suggested as a not improbable explanation of the formation of fulminic acid from ethylic alcohol and nitrous acid. Omitting the metallic salt, the first action may be supposed to occur in the manner represented by the equation:



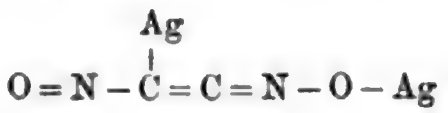
$$\begin{array}{c}CH_3\\|\\CH_2.OH\end{array} + \begin{array}{c}NO.OH\\NO.OH\end{array} = \begin{array}{c}CH_2.NO\\|\\C(N.OH)OH\end{array} + \begin{array}{c}OH_2\\OH_2\end{array}.$$

The compound thus produced is then converted by the loss of the elements of a molecule of water into fulminic acid:

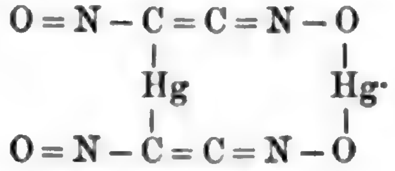


$$\begin{array}{c}CH_2.NO\\|\\C(N.OH)OH\end{array} = OH_2 + \begin{array}{c}CH.NO\\\|\\C(N.OH)\end{array}.$$

If this expression be adopted, the formulæ for argentic and mercuric fulminates would be as follows:



Argentic fulminate.



Mercuric fulminate.

By the action of bromine and iodine on mercuric fulminate, the mercury is displaced by the equivalent amount of bromine and iodine, and the so-called *dibromnitroacetonitrile*, $C_2Br_2N_2O_2$, and *diiodonitracetonitrile*, $C_2I_2N_2O_2$, are produced; both of these are crystalline substances. The bromo-derivative of a compound represented by the expression above given would have the formula $NO-CBr=C=N-OBr$, but such a compound would probably be at once converted by "intramolecular" change into $NO-CBr=CBr-NO$; if this be the case, the bromo-derivative of fulminic acid is a *dinitrosodibromethylene.*

(1223) *Fulminuric acid*, $C_3H_3O_3N_3$.—The preparation of this body from mercuric fulminate has been previously described (1151). It only contains one atom of hydrogen displaceable by metals, but too little is known of its reactions to enable us to represent it by a rational formula. When fulminuric acid is acted upon by a mixture of the strongest nitric and sulphuric acids, a crystalline substance of the composition $C_2N_4O_6$ is produced, which Kekulé considers to be *trinitroacetonitrile*, $C(NO_2)_3CN$. By the action of sulphuretted hydrogen this body is converted into the ammonium derivative of a compound regarded as *dinitroacetonitrile:*

$$C(NO_2)_3CN + 4SH_2 = C(NO_2)_2(NH_4)CN + 2OH_2 + 4S.$$

§ II. Hydrocarbons of the C_nH_{2n}, or Olefine Series.

(1224) The hydrocarbons of this series, which is the second of the isologous series of hydrocarbons, may be regarded as derived from the corresponding paraffins, C_nH_{2n+2}, by the removal of H_2. Hofmann proposed to distinguish the olefines by the termination *ene*, forming the name of the olefine from that of the corresponding paraffin, by changing the termination *ane* into *ene*: as ethane, ethene; in the nomenclature generally adopted, however, the ending is *ylene*, as ethane, ethylene.

Although, hitherto, the series has been but imperfectly investigated, the following terms are known, many of which include isomerides:

Ethylene	C_2H_4	Decylene or Diamylene	$C_{10}H_{20}$
Propylene	C_3H_6	Endecylene	$C_{11}H_{22}$
Butylene or Tetrylene	C_4H_8	Dodecylene or Triisobutylene	$C_{12}H_{24}$
Amylene or Pentylene	C_5H_{10}	Pentadecylene or Triamylene	$C_{15}H_{30}$
Hexylene	C_6H_{12}	Cetene	$C_{16}H_{32}$
Heptylene	C_7H_{14}	Tetramylene	$C_{20}H_{40}$
Octylene	C_8H_{16}	Cerotene	$C_{27}H_{54}$
Nonylene	C_9H_{18}	Melene	$C_{30}H_{60}$

The first three members of the series are gaseous at the ordinary temperature; cerotene and melene are solids, and the remaining terms are liquids.

The compound CH_2 (methylene), which might be supposed to be the first of the series, has never been prepared, neither does it seem to be capable of existing, for in those cases where we might expect to obtain it, ethylene is produced instead; thus:

$$\underset{\text{Diiodomethane.}}{2CH_2I_2} + 4Na = \underset{\text{Ethylene.}}{C_2H_4} + 4NaI.$$

(1225) *Methods of Formation of the Olefines.*—These hydrocarbons, besides occurring amongst the products of the destructive distillation of many organic substances, such as coal, may be produced by a variety of well defined reactions.

1. Olefines are formed by the action of dehydrating agents, such as sulphuric acid, phosphoric anhydride, and zincic chloride, on the alcohols of the ethylic or $C_nH_{2n+1}.OH$ series:

$$C_nH_{2n+1}.OH = C_nH_{2n} + OH_2.$$
$$\underset{\text{Amylic alcohol.}}{C_5H_{11}.OH} = \underset{\text{Amylene.}}{C_5H_{10}} + OH_2.$$

When sulphuric acid is employed, it would seem that the action always takes place in two stages: in the first an acid ethereal sulphate is produced, and this is subsequently resolved into the olefine and sulphuric acid; thus:

$$C_nH_{2n+1}.OH + H_2SO_4 = C_nH_{2n+1}.HSO_4 + OH_2;$$
$$C_nH_{2n+1}.HSO_4 = C_nH_{2n} + H_2SO_4.$$

$$\underset{\text{Ethylic alcohol.}}{C_2H_5.OH} + H_2SO_4 = \underset{\text{Ethylic hydric sulphate.}}{C_2H_5.HSO_4} + OH_2;$$

$$\underset{\text{Ethylic hydric sulphate.}}{C_2H_5.HSO_4} = \underset{\text{Ethylene.}}{C_2H_4} + H_2SO_4.$$

2. By the action of heat on the monohaloid derivatives of the paraffins, or on treating them with an alkali, a molecule of the haloid acid is eliminated and an olefine is formed. In some cases the action of an alkaline hydrate in aqueous or alcoholic solution is sufficient to effect the decomposition, whilst in others, the vapour must be passed over heated lime:

$$C_nH_{2n+1}Cl = C_nH_{2n} + HCl.$$

$$C_2H_5Cl + KHO = C_2H_4 + KCl + OH_2.$$

Chlorethane or Ethylic chloride. Ethylene.

3. Together with a paraffin by the action of some metals on the monohaloid derivatives of the paraffins, as already noticed (p. 130).

4. By the action of the zinc organo-metallic compounds on the monohaloid derivatives of the olefines:

$$Zn(C_mH_{2m+1})_2 + C_nH_{2n-1}Br = C_{n+m}H_{2n+2m} + ZnBrC_nH_{2n+1}.$$

$$Zn(C_2H_5)_2 + C_2H_3Br = C_4H_8 + ZnBrC_2H_5.$$

Zincic ethide. Bromethane or vinylic bromide. Butylene. Zincic bromethide.

5. They are also produced by the action of sodium on a mixture of the monohaloid derivatives of the paraffins and olefines:

$$C_nH_{2n+1}I + C_{2n}H_{2m-1}I + 2Na = C_{n+m}H_{2n+2m} + 2NaI.$$

$$CH_3I + C_3H_5I + 2Na = C_4H_8 + 2NaI.$$

Iodomethane or methylic iodide. α-Iodopropane or allylic iodide. Butylene.

6. By the action of sodium on dihaloid derivatives of the paraffins:

$$C_nH_{2n}Cl_2 + 2Na = C_nH_{2n} + 2NaCl.$$

$$C_5H_{10}Cl_2 + 2Na = C_5H_{10} + 2NaCl.$$

Dichloropentane. Amylene.

7. By the oxidation of the dibasic acids of the succinic or $C_nH_{2n}(COOH)_2$ series, during the electrolysis of their solutions:

$$2C_nH_{2n}(COOH)_2 + O_2 = 2C_nH_{2n} + 4CO_2 + 2OH_2.$$

$$2C_2H_4(COOH)_2 + O_2 = 2C_2H_4 + 4CO_2 + 2OH_2.$$

Succinic acid. Ethylene.

8. In some instances, the organic analogues of ammonic hydrate split up when heated into a tertiary monamine, an olefine and water; thus:

$$(C_2H_5)_4N.OH = (C_2H_5)_3N + C_2H_4 + OH_2.$$

Tetrethylammonic hydrate. Triethylamine. Ethylene.

(1226) *Properties of the Olefines.*—1. The olefines are capable of uniting directly with a molecule of a halogen, and also with iodine and bromine chlorides, ICl, BrCl, and with iodine bromide, BrI, to produce dihaloid derivatives of the paraffins:

$$C_nH_{2n} + X_2 = C_nH_{2n}X_2,$$

where X_2 represents a molecule of a halogen or of a compound of two halogens; thus:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2. \quad C_3H_6 + Br_2 = C_3H_6Br_2.$$

Ethylene. α-Dichlorethane (Ethylenic chloride). Propylene. β-Dibromopropane (Propylenic bromide).

2. The olefines unite with the haloid acids, producing monohaloid derivatives of the paraffins. This combination takes place most readily with hydriodic acid, and more readily with hydrobromic than with hydrochloric acid.

$$C_nH_{2n} + HX = C_nH_{2n+1}X,$$

where HX represents a molecule of the haloid acid.

$$C_3H_6 + HBr = C_3H_7Br. \quad C_4H_8 + HI = C_4H_9I.$$

Propylene. β-Bromopropane (Isopropylic bromide). Butylene. Iodotetrane (Butylic iodide).

The isomeric olefines combine with the haloid acids with very different degrees of readiness: the union being in some cases easily effected by agitating the olefine with a cold saturated solution of the acid, whilst in others it is necessary to heat more or less in order to cause them to combine. This circumstance may afford a convenient means of separating isomeric olefines, and also of indicating the purity of an olefine. It would appear that those of highest boiling-point (the so-called normal olefines) combine least readily, and those of lowest boiling-point at the opposite extremity of the isomeric series most readily, the intermediate terms being also intermediate in their behaviour with haloid acids.

3. They also unite directly with hypochlorous acid, forming monochlorinated monohydric alcohols or glycollic chlorhydrins:

$$C_nH_{2n} + ClOH = C_nH_{2n}Cl.OH.$$

$$C_2H_4 + ClOH = C_2H_4Cl.OH.$$

Ethylene. Monochlorethylic alcohol.

These chlorinated alcohols are readily converted into alcohols of the ethylic or $C_nH_{2n+1}.OH$ series, by the action of nascent hydrogen.

4. The olefines unite with sulphuric acid, forming acid ethereal sulphates:

$$C_nH_{2n} + H_2SO_4 = C_nH_{2n+1}.HSO_4.$$

$$C_2H_4 + H_2SO_4 = C_2H_5.HSO_4.$$

Ethylene. Hydric ethylic sulphate.

These sulphates when distilled with water, yield sulphuric acid and the corresponding alcohols of the ethylic series:

$$C_nH_{2n+1}.HSO_4 + OH_2 = H_2SO_4 + C_nH_{2n+1}.OH.$$

$$\underset{\text{Hydric ethylic sulphate.}}{C_2H_5.HSO_4} + OH_2 = H_2SO_4 + \underset{\text{Ethylic hydrate.}}{C_2H_5.OH.}$$

The experiments hitherto made appear to indicate that the combination of the olefines with the haloid acids, with hypochlorous acid, and with sulphuric acid, is governed by a very simple law, which is that the more negative radicle (X′) of the compound (HX′) entering into union with the olefine, always attaches itself to the least hydrogenized carbon atom. Thus in the case of propylene the following reactions have been observed:

$$\underset{\text{Propylene.}}{CH_3.CH{=}CH_2} + HI = \underset{\text{Isopropylic iodide.}}{CH_3.CHI.CH_3.}$$

$$\underset{\text{Propylene.}}{CH_3.CH{=}CH_2} + Cl.OH = \underset{\text{Chloropropylic alcohol.}}{CH_3.CHCl.CH_2(OH).}$$

$$\underset{\text{Propylene.}}{CH_3.CH{=}CH_2} + H_2SO_4 = \underset{\text{Isopropylic hydric sulphate.}}{CH_3.CH(HSO_4).CH_3.}$$

All of these, it will be observed, are in accordance with the general equation:

$$CH_3.CH{=}CH_2 + HX' = CH_3.CHX'.CH_3,$$

and it is probable that the combination of the olefines with other compounds follows the same general law.

5. The action of oxidizing agents on the olefines varies with the nature of the reagent employed, and the conditions of experiment. Thus, according to Chapman and Thorp (*Journ. Chem. Soc.*, 1866, xix. 491), a solution of potassic dichromate, to which sufficient sulphuric acid is added to form chromic sulphate with the chromium and hydric potassic sulphate with the potassium, oxidizes ethylene, C_2H_4, to carbonic anhydride and water, and converts amylene, C_5H_{10}, from fermentation amylic alcohol, into acetic acid, carbonic anhydride, and water:

$$\underset{\text{Amylene.}}{C_5H_{10}} + 7O = \underset{\text{Acetic acid.}}{2C_2H_4O_2} + CO_2 + OH_2.$$

Hexylene, C_6H_{12}, from mannite, yields propionic and acetic acids, carbonic anhydride and water:

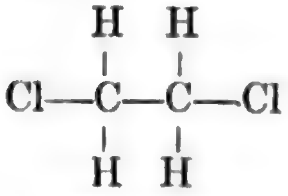
$$\underset{\text{Hexylene.}}{C_6H_{12}} + 7O = \underset{\text{Propionic acid.}}{C_3H_6O_2} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + CO_2 + OH_2.$$

Similar results are obtained with a solution of potassic permanganate acidulated with sulphuric acid.

Truchot states, however (*Compt. Rend.*, lxiii. 274), that a solution of pure potassic permanganate oxidizes ethylene to formic acid, carbonic anhydride and water, and propylene, C_3H_6, to acetic acid, formic acid, and water, whilst amylene yields butyric, propionic, acetic, and formic acids. According to Berthelot (*Compt. Rend.*, lxiv. 35), an alkaline solution of potassic permanganate converts ethylene into oxalic acid, $C_2H_2O_4$, producing also formic acid and carbonic anhydride; propylene is said to furnish malonic acid, $C_3H_4O_4$, together with oxalic, acetic, and formic acids; and amylene appears to yield pyrotartaric acid, $C_5H_8O_4$, besides succinic, malonic, and oxalic acids, and various acids of the acetic series. Berthelot also states (*ibid.*, lxviii. 334), that when a solution of pure chromic acid is employed, ethylene is converted into aldehyde, C_2H_4O; whilst propylene furnishes a notable quantity of propionic acid, $C_3H_6O_2$, besides acetone, C_3H_6O, and acetic acid; amylene, when similarly treated, yields together with neutral products, a mixture of acids of the acetic series, containing a considerable quantity of valeric acid, $C_5H_{10}O_2$, also butyric, propionic, and acetic acids, and a small quantity of formic acid.

6. The olefines undergo polymerization with great facility; thus amylene, C_5H_{10}, from fermentation amylic alcohol, when it is added to concentrated sulphuric acid, or warmed with zincic chloride, is almost entirely converted into its polymerides diamylene, $C_{10}H_{20}$, triamylene, $C_{15}H_{30}$, and tetramylene, $C_{20}H_{40}$.

(1227) *Isomerism of the Olefines.*—Although at present comparatively little is known of the olefines, it appears probable that they may all be represented as derived from ethylene, $H_2C{=}CH_2$, by the substitution of the so-called monad positive radicles C_nH_{2n+1} for one or more atoms of hydrogen. According to this view only one propylene, C_3H_6, is possible, having the formula $H_2C{=}CH(CH_3)$. If, however, the hypothesis be adopted that an olefine is capable of existing, corresponding to each of the isomeric dihaloid derivatives of the paraffins, there would be two ethylenes corresponding to the two dichlorethanes; thus:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Cl & — & C & — & C & — & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

α-Dichlorethane. (Ethylenic chloride).

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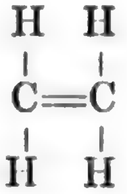

$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Ethylene.

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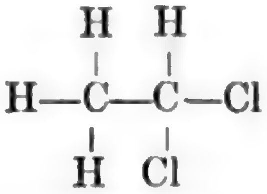

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & Cl \\ & & | & & | & & \\ & & H & & Cl & & \end{array}$$

β-Dichlorethane. (Ethylidenic chloride).

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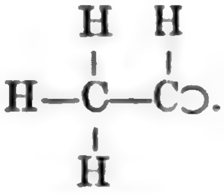

$$\begin{array}{ccccc} & & H & & H \\ & & | & & | \\ H & — & C & — & C\supset. \\ & & | & & \\ & & H & & \end{array}$$

Ethylidene.

Similarly there would be no less than four propylenes.* As a matter of fact, however, only one ethylene and one propylene have been isolated. In like manner, the former hypothesis supposes the existence of but three butylenes: $H_2C{=}CH(C_2H_5)$; $H_2C{=}C(CH_3)_2$; and $(CH_3)HC{=}CH(CH_3)$, whilst the latter permits no less than nine modifications.

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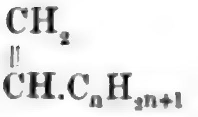
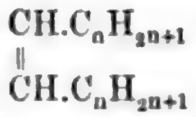
* The number of possible olefines also becomes largely increased if it be assumed, that not only may two of the atoms of carbon in each olefine be united

If the olefines be regarded as derived from ethylene, they may be divided into groups, in which one, two, three, or four atoms of the hydrogen in the ethylene are displaced by radicles of the form C_nH_{2n+1}, as follows:



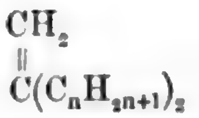
$$\begin{array}{l} CH_2 \\ \| \\ CH.C_nH_{2n+1} \end{array};$$

GROUP I.



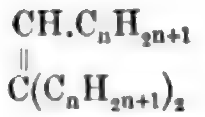
$$\begin{array}{l} CH.C_nH_{2n+1} \\ \| \\ CH.C_nH_{2n+1} \end{array};$$

GROUP II.



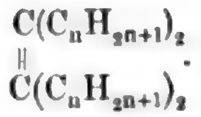
$$\begin{array}{l} CH_2 \\ \| \\ C(C_nH_{2n+1})_2 \end{array};$$

GROUP III.



$$\begin{array}{l} CH.C_nH_{2n+1} \\ \| \\ C(C_nH_{2n+1})_2 \end{array};$$

GROUP IV.



$$\begin{array}{l} C(C_nH_{2n+1})_2 \\ \| \\ C(C_nH_{2n+1})_2 \end{array}.$$

GROUP V.

Each of these five groups may be again subdivided, according to the nature of the C_nH_{2n+1} radicles.

The Table on the following pages contains a list of the few olefines at present known, to which rational formulæ may be assigned with more or less confidence. The formulæ there given are, however, in many cases, merely those which appear most probable, as much experimental evidence is still wanting to render our knowledge of this series at all satisfactory.

(1228) ETHYLENE OF ETHENE.—*Olefiant Gas, Heavy Carburetted Hydrogen,* or *Elayl.* $C_2H_4=28.H_2C{=}CH_2$. — This gas is formed together with other hydrocarbons during the destructive distillation of coal, and of many resinous and fatty bodies; it is one of the most important luminous constituents of coal-gas. Berthelot has shown that it is present in small quantity amongst the products of the destructive distillation of baric formate, $(HCO_2)_2Ba$, and also that it is formed

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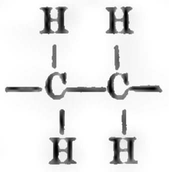
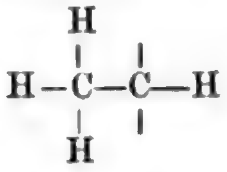
by two affinities of each, as expressed by the formula $H_2C=CH_2$, or the two affinities of a single atom of carbon satisfy each other as in $H_3C{-}\boxed{CH}$, but that free affinities may exist as represented by the formulæ:



$$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ -C-C- \\ |\ \ \ | \\ H\ \ H \end{array};$$



$$\begin{array}{c} H\ \ \ \ \ \\ |\ \ \ | \\ H-C-C-H \\ |\ \ \ | \\ H\ \ \ \ \ \end{array}$$

At present, however, there does not appear to be any evidence in favour of this assumption.

Table of Homologous

		Series $CH_2 \Vert CH(C_nH_{2n+1})$.		Series $CH(C_nH_{2n+1} \Vert CH(C_nH_{2n+1})$.	
		Formula.	B.P. (Cent.)	Formula.	B. P.
C_2H_4	Ethylene	$CH_2 : CH_2$	—		
C_3H_6	Propylene	$CH_2 : CH(CH_3)$	—		
C_4H_8	Butylene	$CH_2 : CH(C_2H_5)$	?	$CH(CH_3) : CH(CH_3)$	3°
C_5H_{10}	Amylene	$CH_2 : CH(C_3H_7)^\alpha$ $CH_2 : CH(C_3H_7)^\beta$	abt. 40° „ 25°	$CH(CH_3) : CH(C_2H_5)$	36°
C_6H_{12}	Hexylene	$CH_2 : CH(C_4H_9)^\alpha$ $CH_2 : CH(C_4H_9)^\delta$	„ 67° „ 70°	...	...
C_7H_{14}	Heptylene	$CH_2 : CH(C_5H_{11})^\alpha$	...	...	...
C_8H_{16}	Octylene	$CH_2 : CH(C_6H_{13})^\alpha$	126°		
C_9H_{18}	Nonylene				
$C_{10}H_{20}$	Decylene	...	...	...	...
$C_{11}H_{22}$	Endecylene	$CH_2 : CH(C_9H_{19})^\alpha$	200°		
$C_{12}H_{24}$	Dodecylene	...	...	...	...
$C_{13}H_{26}$	Tridecylene				
$C_{14}H_{28}$	Tetradecylene				
$C_{15}H_{30}$	Pentadecylene (Triamylene)				
$C_{16}H_{32}$	Hexadecylene (Cetene)				
$C_{20}H_{40}$	Tetramylene				
$C_{27}H_{54}$	Ceroteno				
$C_{30}H_{60}$	Melene				

together with methane, on passing sulphuretted hydrogen mixed with the vapour of carbonic disulphide over copper heated to dull redness; very little ethylene is obtained, however, the gaseous product being chiefly hydrogen.

Ethylene is also produced by the action of sodium on diiodomethane, CH_2I_2; by heating methylic alcohol, $CH_3.OH$, with phosphoric anhydride; and by the action of sodium on α-diiodethane, and on α- and β-dichlorethane. Whilst α-dichlorethane, however, is readily attacked by sodium at a temperature below the melting-point of the latter, β-dichlorethane may be distilled over the metal without change, and is only acted upon when the two are heated together to about 100° (212° F.). The monohaloid derivatives of the paraffin ethane, C_2H_6, yield ethylene when passed through a tube heated to dull redness; and it *and Isomeric Olefines.*

Series $\begin{array}{c}CH_2\\ \Vert\\ C(C_nH_{2n+1})_2\end{array}$.		Series $\begin{array}{c}CH(C_nH_{2n+1})\\ \Vert\\ C(C_nH_{2n+1})_2\end{array}$.		Series $\begin{array}{c}C(C_nH_{2n+1})_2\\ \Vert\\ C(C_nH_{2n+1})_2\end{array}$.	
Formula.	B. P.	Formula.	B. P.	Formula.	B. P.
$CH_2 : C(CH_3)_2$	−7°				
...	...	$CH(CH_3) : C(CH_3)_2$	35°		
...	...	$CH(CH_3) : C(CH_3)(C_2H_5)$	68°—72°		
$CH_2 : C(CH_3)(C_4H_9)^{\delta}$	78°—80°	$CH(CH_3) : C(C_2H_5)_2$ $CH(C_3H_7)^{\beta} : C(CH_3)_2$	— 83°		
...	...	...	...	$C(CH_3)(C_3H_7)^{\beta} : C(CH_3)(C_3H_7)^{\beta}$ (Diamylene).	150°—153°
...	...	...	...	$C(CH_3)(C_4H_9)^{\delta} : C(CH_3)(C_4H_9)^{\delta}$ (? Triisobutylene).	173°—176°

is also formed when iodethane or ethylic iodide, C_2H_5I, is heated with an alcoholic solution of potassic hydrate; the amount produced, however, is extremely small in the latter case.

Kolbe has shown (*Ann. Chem. Pharm.*, cxxxi. 79), that when a solution of sodic succinate is submitted to electrolysis, ethylene is evolved at the positive pole, together with carbonic anhydride.

$$\underset{\text{Sodium succinate.}}{C_2H_4(CO_2Na)_2} + OH_2 = \underset{\text{Ethylene.}}{C_2H_4} + CO_2 + Na_2CO_3 + H_2.$$

A very interesting mode of formation is by the action of nascent hydrogen on acetylene, C_2H_2. For this purpose cuprous acetylide (*vide* acetylene) is added to a mixture of zinc and dilute ammonia, and the whole gently warmed. The hydrogen liberated by the action of the zinc on the ammonia, unites with the acetylene from the cuprous acetylide, to produce ethylene: $C_2H_2 + H_2 = C_2H_4$.

Ethylene is usually prepared by heating ethylic alcohol with concentrated sulphuric acid. For this purpose, a mixture of 1 measure of alcohol and 4 measures of sulphuric acid may be gently warmed in a capacious glass flask or retort; at first the gas comes off freely, but after a time the mixture begins to blacken, and finally becomes thick, and froths up considerably, so that the operation requires careful watching in its latter stages. This tendency to froth may be much diminished by adding sufficient sand to the liquid to form a thin paste. The ethylene thus obtained is accompanied by the vapours of alcohol and ether, and towards the close of the process by sulphurous anhydride in large quantity.

The reaction which takes place may be thus explained. The alcohol is acted upon by the sulphuric acid, and the hydric ethylic sulphate which is formed is decomposed at a high temperature into ethylene and sulphuric acid:

$$\underset{\text{Ethylic alcohol.}}{C_2H_5.OH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethylic hydric sulphate.}}{C_2H_5.HSO_4} + OH_2;$$

and when heated:

$$\underset{\text{Ethylic hydric sulphate.}}{C_2H_5.HSO_4} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

The liberated sulphuric acid is capable of again converting alcohol into hydric ethylic sulphate, which, in its turn, is decomposed into ethylene and sulphuric acid. In fact, on dropping alcohol into a mixture of about 30 measures of sulphuric acid and 9 of water, maintained at a temperature of 160°—165° (320°—330° F.), an effervescence of the acid liquid takes place, and water and ethylene gas pass over. In this way a small quantity of sulphuric acid is sufficient to decompose a relatively large quantity of alcohol.

When, however, a considerable quantity of ethylene is required in a continuous current, the following is the best process:—

A mixture of 25 grms. of alcohol and 150 grms. of sulphuric acid is placed in a glass flask of 2 or 3 litres in capacity, and the neck of this flask is provided with a cork, through which are inserted a bent glass tube and a tap-funnel. The mixture is now heated on the sand-bath until a continuous stream of the gas is evolved, when the tap of the funnel is partly opened, and a cooled mixture of equal parts of alcohol and sulphuric acid is allowed to drop in slowly. By carefully regulating the temperature, and the rate of the flow of liquid through the tap, a constant current of ethylene may readily be obtained. (Erlenmeyer a. Bunte, *Ann. Chem. Pharm.*, clxviii. 64).

The crude gas prepared by these methods should be passed first into an empty Woulffe's bottle, then through a solution of potassic or sodic hydrate, and finally through concentrated sulphuric acid; in this way it is deprived of the sulphurous anhydride and of the vapours of alcohol and ether which accompany it.

Ethylene is a transparent and colourless gas; it has a faint, sweetish, alliaceous odour, and is soluble in about 12 times its bulk of cold water. It was liquefied by Faraday under great pressure, but remained unfrozen at −110° (−166° F.). Ethylene does not support combustion, but is itself very inflammable, burning with a white luminous flame, which deposits carbonaceous matter abundantly upon cold bodies introduced into it. If passed through a porcelain tube heated to bright redness it is decomposed: half its carbon is deposited, and methane or marsh gas is formed, which occupies the same volume as that of the ethylene from which it was produced. If the temperature to which the gas is exposed be very high, all the carbon is deposited, each volume of gas yielding 2 volumes of hydrogen.

The composition of ethylene may be ascertained by detonation with oxygen; the explosion, however, is very powerful, and requires care, otherwise the eudiometer will be broken. One volume of the gas requires for its complete combustion 3 volumes of oxygen; 2 volumes of carbonic anhydride remain and represent 2 out of the 3 volumes of oxygen, whilst the other volume of oxygen combines with 2 volumes of hydrogen furnishing 2 volumes of steam, which become condensed: 2 volumes of ethylene, therefore, contain 4 volumes of hydrogen or 4 parts by weight united with 24 parts of carbon or what may be 2 volumes of carbon vapour, $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. From these data the composition of the gas may be represented in the following manner:

			By weight.		By vol.
Carbon	$C_2 =$	24 or	85·71	...	?
Hydrogen	$H_4 =$	4	14·29	...	4
Ethylene	$C_2H_4 =$	28	100·00		2

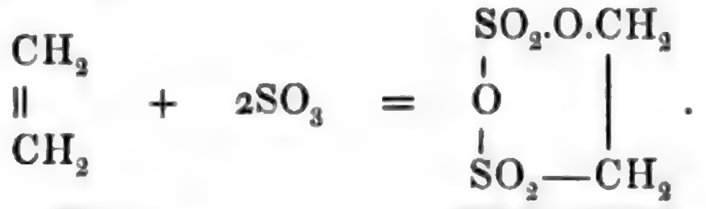
Ethylene is slightly soluble in alcohol, in oil of turpentine, and in the fixed oils; ether dissolves it more freely. It is also soluble in cuprous chloride solution. It combines with sulphuric anhydride; hence it is completely absorbed by fuming sulphuric acid, and is somewhat soluble in ordinary sulphuric acid. Ethylene, when mixed with an equal volume of chlorine, unites with it and becomes condensed to a heavy, sweetish, aromatic liquid, which collects into oily-looking drops, heavier than water: it was owing to this reaction that the name of olefiant (or oil-producing) gas was given to it, and the oily body itself was commonly known as *Dutch Liquid*, from the circumstance of its discovery in Holland. If 1 measure of ethylene be mixed with 2 measures of chlorine, the mixture will burn quietly on the application of a light, depositing the whole of the carbon of the gas in the form of a dense smoke, whilst the hydrogen unites with the chlorine to form hydrochloric acid. It also combines with bromine and iodine. Ethylene, when heated with a saturated solution of hydriodic acid to 100° (212° F.) unites with it, forming iodethane or ethylic iodide, C_2H_5I; it also combines, but less readily, with hydrobromic acid; and still less readily with hydrochloric acid.

Ethylene unites directly with hydrogen producing ethane, C_2H_6, when a mixture of equal volumes of the two gases is placed in contact with platinum-black (v. Wilde, *Deut. chem. Ges. Ber.*, vii. 353).

When briskly agitated with ordinary concentrated sulphuric acid, ethylene is slowly absorbed by it, forming hydric ethylic sulphate: $C_2H_4+H_2SO_4=C_2H_5.HSO_4$ (Berthelot); if, however, the acid be heated to 160°—170° (320°—338° F.), the combination takes place readily, and considerable quantities of ethylic hydric sulphate may thus be prepared (Butlerow a. Goriainow, *Ann. Chem. Pharm.*, clxix. 146). This reaction is of great interest, for on distilling hydric ethylic sulphate with water, alcohol is produced; and since ethylene may be obtained from acetylene, and the latter can be formed by the direct union of carbon and hydrogen, it is possible in this way to build up ethylic alcohol from its constituent elements.

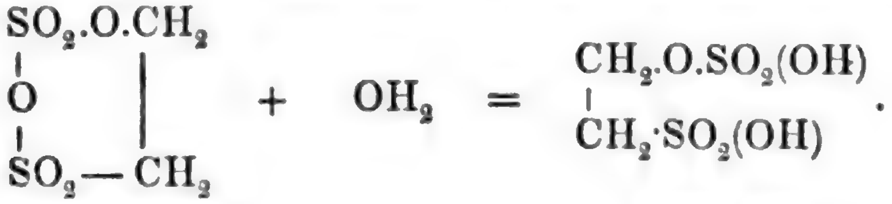
In order to combine ethylene with sulphuric acid, Butlerow uses the following apparatus. The inner tube of a Liebig's condenser, about 1 cm. wide and ·5 to ·6 of a metre long, is filled with coarsely-powdered glass, and closed at each end by a caoutchouc stopper pierced by two openings. A delivery tube and a glass tap-funnel, through which sulphuric acid is introduced, are passed through the upper stopper; the lower stopper carries a tube extending ·1 metre up into the powdered glass, through which the gas is introduced, and a second tube terminating immediately above the stopper, through which the acid flows away. The latter tube, however, is bent outside the condenser-tube so that when the bend is filled with sulphuric acid, a valve is formed which prevents the escape of gas. The inner tube of the condenser is heated by a current of the vapour of boiling turpentine, or some other vapour of suitable temperature, which circulates in the annular space between the two tubes of the condenser; and whilst sulphuric acid is slowly admitted above through the tap-funnel a current of ethylene is passed in from below.

Ethylene combines readily with sulphuric anhydride, forming *ethionic anhydride*:



Ethylene. Ethionic anhydride.

And this, by contact with water, is converted into ethionic acid:



Ethionic anhydride. Ethionic acid.

Chlorhydric sulphate, $ClSO_2.OH$, also readily unites with ethylene, forming the compound $ClSO_2.OC_2H_5$.

Ethylene combines with hypochlorous and hypobromous acids, forming the compounds $C_2H_4Cl.OH$ and $C_2H_4Br.OH$, and also with Schützenberger's chlorine acetate:

$$C_2H_4 + CH_3.COOCl = CH_3.COO(C_2H_4Cl).$$

Ethylene. Chlorine acetate. Chlorethylic acetate or Glycollic acetochlorhydrin.

According to Carius (*Ann. Chem. Pharm.*, cxxvi. 209), ethylene unites with hydric peroxide, $(OH)_2$, forming glycol, $C_2H_4(OH)_2$; the conditions, however, under which this interesting reaction takes place have not been made known.

Besides those already enumerated, ethylene unites with many other compounds, such as the chlorides of sulphur, SCl_2 and S_2Cl_2, forming the compounds $C_2H_4Cl_2S$ and $C_4H_8Cl_2S_2$; with Schützenberger's platoso-carbonyl chloride, $COPtCl_2$, forming $COPtCl_2C_2H_4$; and with platinous chloride, $PtCl_2$, forming $PtCl_2C_2H_4$ (Birnbaum, *Ann. Chem. Pharm.*, cxlv. 67). This last compound may also be obtained by heating platinic chloride with alcohol; and by heating ether with ferric chloride, Kachler (*Deut. chem. Ges. Ber.*, ii. 510) has obtained a compound of ethylene with ferrous chloride, $FeCl_2C_2H_4$. Compounds of ethylene with iridium chloride and potassic or ammonic chloride are also known, viz., $IrCl_4(C_2H_4)_2(KCl)_2$ and $IrCl_4(C_2H_4)_2(NH_4Cl)_2$. All these various compounds may be regarded as formed by reactions, similar to those indicated in the following general equations:

$$(C_2H_4)'' \div XCl_n = (C_2H_4Cl)'XCl_{n-1}.$$

$$C_2H_4 + SCl_2 = (C_2H_4Cl)SCl.$$

$$2(C_2H_4)'' + XCl_n = \left.\begin{matrix}(C_2H_4Cl)'\\(C_2H_4Cl)'\end{matrix}\right\} XCl_{n-2}.$$

$$2C_2H_4 + S_2Cl_2 = (C_2H_4Cl)_2S_2.$$

When ethylene is passed into liquid nitric peroxide, N_2O_4, a crystalline body of the composition $C_2H_4N_2O_4$ is produced; whilst by passing it into a well-cooled mixture of concentrated nitric and sulphuric acids, the compound $C_2H_4N_2O_5$ is formed. The latter is a colourless oil, of very pungent odour, which yields glycol when heated with aqueous hydriodic acid; it would appear, therefore, to be a glycollic nitrate nitrite:

$$C_2H_4\left\{\begin{matrix}O.NO\\O.NO_2\end{matrix}\right. + 4HI = C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + 2NO + 2I_2 + OH_2.$$

Glycollic nitrate nitrite. Glycol.

(1229) *Polymerization of Ethylene.*—When ethylene is submitted to the action of the silent electric discharge it becomes condensed into a liquid (P. a. A. Thenard; v. Wilde, *Deut. chem. Ges. Ber.*, vii. 355). Polymerides of ethylene are also formed, although in small quantity, in the preparation of the gas from alcohol and sulphuric acid, and in larger quantity by the destructive distillation of the ethyl sulphates. Thus when potassic ethylic sulphate is distilled, not only is ethylene given off, but a liquid polymeride is also obtained:

$$C_2H_5.KSO_4 = C_2H_4 + KHSO_4.$$

Potassic ethylic sulphate. Ethylene.

On cooling this liquid, a crystalline polymeride of ethylene, the so-called *etherin*, separates. It melts at 110° (230° F.) and boils at 260° (320° F.).

(1230) PROPYLENE or PROPENE. — *Methyl-ethylene* $C_3H_6 = 42$. $H_2C{=}CH(CH_3)$—This hydrocarbon is present in coal-gas, and occurs amongst the products of the destructive distillation of many organic bodies. According to Berthollet, a mixture of carbonic oxide and methane yields propylene when passed through a red hot tube: $2CH_4 + CO = C_3H_6 + OH_2$. Propylene was first obtained by Reynolds in 1851 by passing the vapours of fermentation amylic alcohol, $C_5H_{11}.OH$, through a tube heated to redness; it is also produced in considerable quantity when a mixture of 10 parts of oleic acid, 3 of potassic hydrate, and 3 of soda-lime is submitted to destructive distillation. Propylene may be obtained by heating α- and β-iodopropane (primary and secondary or isopropylic iodide) with an alcoholic solution of potassic hydrate:

$$CH_3.CH_2.CH_2I + KHO = CH_3.CH{=}CH_2 + KI + OH_2.$$

α-Iodopropane. Propylene.

$$CH_3.CHI.CH_3 + KHO = CH_3.CH{=}CH_2 + KI + OH_2.$$

β-Iodopropane. Propylene.

With the secondary iodide, the action takes place at 40°—50° (104°—122° F.), but the primary iodide is not attacked until heated to a somewhat higher temperature. It is also formed by the action of nascent hydrogen from zinc and glacial acetic acid on β-dibromopropane or propylenic bromide:

$$CH_3.CHBr.CH_2Br + H_2 = CH_3.CH{=}CH_2 + 2HBr.$$

The isomeric γ-dibromopropane or methylbromacetol furnishes propane (Linnemann, *Ann. Chem. Pharm.*, clxi. 43). According to Reboul, the 3 isomeric dibromopropanes (1189) furnish the same propylene when heated with sodium, but the β and γ compounds are far more readily decomposed than α-dibromopropane, which requires heating with sodium to 160° (320° F.).

Propylene is best prepared, however, by bringing the α-iodopropylene or allylic iodide in contact with zinc and hydrochloric acid:

$$2H_2C{=}CH.CH_2I + 2Zn + 2HCl = 2H_2C{=}CH.CH_3 + ZnI_2 + ZnCl_2;$$

or by the action of fused zincic chloride on isopropylic alcohol, $CH_3.CH(OH).CH_3$. The mixture of the alcohol with $2\frac{1}{2}$ times its weight of zincic chloride is allowed to stand 24 hours, and then heated gently on the sand-bath, when a regular evolution of gas takes place (Friedel a. Silva). The action of hydriodic acid on allylic iodide also gives rise to the formation of propylene.

Propylene, like ethylene, is a colourless gas, condensible to a liquid by strong pressure: absolute alcohol dissolves 12 to 13 times its volume of the gas. Propylene combines readily with chlorine and bromine, and also unites with iodine (1183, 1194). It combines with the haloid acids and with sulphuric acid far more readily than ethylene: in these cases β-derivatives of propane or secondary or isopropylic compounds are always formed; thus:

$$\underset{\text{Propylene.}}{CH_2{=}CH.CH_3} + HI = \underset{\substack{\beta\text{-Iodopropane}\\ \text{or isopropylic iodide.}}}{CH_3.CHI.CH_3}.$$

$$\underset{\text{Propylene.}}{CH_2{=}CH.CH_3} + H_2SO_4 = \underset{\text{Isopropylic hydric sulphate.}}{CH_3.CH(HSO_4).CH_3}.$$

Markownikoff has stated (*Ann. Chem. Pharm.*, cliii. 237) that propylene unites with hypochlorous acid, forming monochlorinated secondary propylic alcohol:

$$CH_2{=}CH.CH_3 + ClHO = CH_2Cl.CH(OH).CH_3;$$

but Henry, who has recently examined this reaction, finds that monochlorinated *primary* propylic alcohol is produced (*Compt. Rend.*, lxxix. 1258):

$$\underset{\text{Propylene.}}{CH_2{=}CH.CH_3} + ClOH = \underset{\text{Chloropropylic alcohol.}}{CH_2(OH).CHCl.CH_3}.$$

Propylene readily undergoes polymerization: thus the hydric isopropylic sulphate formed by the union of propylene with sulphuric acid gradually decomposes, even at the ordinary temperature, into sulphuric acid and polymerides of propylene; likewise, when a mixture of propylene and gaseous boric fluoride is allowed to stand over mercury, the propylene gradually condenses into a liquid.

(1231) **Butylene** or **Butene**.—*Tetrylene*, $C_4H_8 = 56$.—An olefine of the composition C_4H_8 was first discovered by Faraday amongst the gases obtained by the destructive distillation of oil, and on this account it long went by the name of oil-gas. Butylenes have been prepared by various methods, but the statements with regard to their properties are somewhat conflicting.

α- or *Normal Butylene.—Ethyl-ethylene*, $H_2C{=}CH(C_2H_5)$.—Wurtz found that a mixture of iodomethane and α-iodopropylene or allylic iodide diluted with ether, when heated to 100° (212° F.) with sodium in strong glass tubes, yielded this hydrocarbon:

$$CH_3I + H_2C{=}CH.CH_2I + 2Na = H_2C{=}CH.CH_2.CH_3. + 2NaI.$$

The boiling-point of the product lay between − 6° and + 6° (21°·2 and 42°·8 F.). With bromine it yields a dibromotetrane, $C_4H_8Br_2$, boiling at 159° (318°·2 F.); whilst with hydriodic acid it forms a secondary butylic iodide:

$$CH_2{=}CH.C_2H_5 + HI = CH_3.CHI.C_2H_5.$$

When normal primary butylic iodide is heated with an alcoholic solution of potassic hydrate, much ethylbutyl ether is produced, but at the same time some butylene is formed (Saytzeff, *Journ. pr. Chem.* [2] iii. 88). The boiling-point of this butylene was not determined, nor was its bromide examined, but it is probably α-butylene formed in the following manner:

$$\underset{\text{Primary butylic iodide.}}{CH_3.CH_2.CH_2.CH_2I} + KHO = \underset{\text{α-Butylene.}}{CH_3.CH_2.CH{=}CH_2} + KI + OH_2.$$

It yields secondary butylic iodide when combined with hydriodic acid.

By the action of zincic ethide at 140° (284° F.) on bromethylene or vinylic bromide, Wurtz obtained a butylene boiling between −8° and 0° (17°·6 and 32° F.), which combined with bromine to form a dibromotetrane, $C_4H_8Br_2$, boiling at 166° (330°·8 F.) From the mode of formation, there is reason to suppose that the hydrocarbon thus prepared is α-butylene, thus:

$$\underset{\text{Bromethylene.}}{CH_2{=}CHBr} + \underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} = \underset{\text{α-Butylene.}}{CH_2{=}CH{\cdot}C_2H_5} + \underset{\text{Zincic bromethide.}}{ZnBrC_2H_5}.$$

The boiling-point of the dibromotetrane which it yields, differs, however, considerably from that of the dibromotetrane prepared from allylic iodide. Either, therefore, an isomeric change must have taken place during the formation of one of these hydrocarbons, or the dibromotetranes were not both obtained in a state of purity; the latter appears to be the more probable explanation.

β-Butylene, Dimethyl-ethylene, $CH_3.HC{=}CH.CH_3$.—Secondary butylic iodide readily furnishes a butylene, when acted upon by an alcoholic solution of potassic hydrate, which is probably a dimethyl-ethylene of the above form, since it yields a chlorinated *secondary* butylic alcohol when combined with hypochlorous acid:

$$CH_3.CH_2.CHI.CH_3 + KHO = CH_3.HC.{=}CH.CH_3 + KI + OH_2.$$

$$CH_3.HC{=}CH.CH_3 + ClOH = CH_3.CHCl.CH(OH).CH_3.$$

According to De Luynes, the butylene thus prepared boils at 3° (37°·4 F.), and solidifies to a crystalline mass when cooled in a mixture of ether and carbonic anhydride in vacuo; with hydriodic acid it yields secondary butylic iodide. It forms with bromine a dibromotetrane which boils at 159° (318°·2 F.) (Lieben).

γ-Butylene; Dimethyl-ethylene, $(CH_3)_2C{=}CH_2$.—Very little butylene is obtained when isoprimary and tertiary butylic alcohols are treated with sulphuric acid or zincic chloride, the greater portion undergoing polymerization at the moment of formation; by the action, however, of an alcoholic solution of potassic hydrate on the butylic iodides prepared from these alcohols, an almost theoretical yield of so-called isobutylene is obtained:

$$\underset{\text{Isoprimary butylic iodide.}}{CH(CH_3)_2.CH_2I} + KHO = \underset{\text{γ-Butylene.}}{C(CH_3)_2{=}CH_2} + KI + OH_2.$$

$$\underset{\text{Tertiary butylic iodide.}}{C(CH_3)_3I} + KHO = \underset{\text{γ-Butylene.}}{C(CH_3)_2{=}CH_2} + KI + OH_2.$$

It is also produced when the vapours of fermentation amylic alcohol are passed through a red-hot tube, and by the electrolysis of an aqueous solution of potassic isovalerate, in the latter case accompanied by diisobutyl.

It may be condensed to a colourless liquid, which boils at about −7° (19°·4 F.) It is entirely absorbed by a concentrated cold aqueous solution of hydriodic acid, with which it unites more readily than α-butylene, and forms δ-iodotetrane or tertiary butylic iodide:

$$C(CH_3)_2{=}CH_2 + HI = C(CH_3)_3I.$$

When isobutylene is enclosed in a tube with concentrated hydrochloric acid, and the mixture heated to 100° (212° F.), it is entirely converted into δ-chlorotetrane or tertiary butylic chloride. It is also absorbed by a mixture of 3 pts. concentrated sulphuric acid and 1 pt. water, and partially converted into tertiary butylic hydric sulphate, $C(CH_3)_3.HSO_4$. A considerable portion, however, undergoes polymerization, a colourless oil being produced, which consists chiefly of *triisobutylene*, $C_{12}H_{24}$, boiling at 173°—176° (343°·4—348°·8 F.). According to De Luynes, α-butylene is also readily polymerized by sulphuric acid.

Isobutylene combines with hypochlorous acid, forming monochlorinated isoprimary butylic alcohol:

$$C(CH_3)_2{=}CH_2 \;+\; ClOH \;=\; CCl(CH_3)_2.CH_2(OH).$$

This result, it will be seen, is in accordance with the law previously enunciated, that the more negative radicle of the compound uniting with an olefine attaches itself to the least hydrogenized carbon atom. According to Saytzeff, however, butylene from primary butylic iodide produces monochlorinated secondary butylic alcohol when combined with hypochlorous acid; if this butylene be correctly represented by the formula above given, the result would not be in accordance with the law in question, which requires the formation of a chlorinated primary butylic alcohol:

$$CH_2{=}CH\;C_2H_5 \;+\; ClOH \;=\; CH_2(OH).CHCl.C_2H_5.$$

(1232) AMYLENE, PENTYLENE OR PENTENE: $C_5H_{10} = 70$.—Several amylenes have been obtained, but as yet they have been but imperfectly investigated.

Normal or *α-Amylene, Propylethylene:* $CH_2{=}CH.CH_2.CH_2.CH_3$ or $CH_2{=}CH(C_3H_7)^{\alpha}$.—Wurtz prepared this hydrocarbon by acting on allylic iodide with zincic ethide:

$$\underset{\text{Allylic iodide.}}{CH_2{=}CH.CH_2I} \;+\; \underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} \;=\; \underset{\alpha\text{-Amylene.}}{CH_2{=}CH.CH_2.C_2H_5} \;+\; ZnIC_2H_5.$$

Its boiling-point lies between 35° and 40° (95°—104° F.), but has not been accurately determined, as the amylene can only be separated with difficulty from the pentane and other hydrocarbons produced at the same time. When the mixture of chloropentanes obtained on chlorinating normal pentane is decomposed with potassic acetate, it yields a considerable quantity of pentylene boiling at 39°—40° (102°·2—104° F.) (Schorlemmer); this product undoubtedly contains α-amylene, but probably mixed with an isomeric olefine. α-Amylene combines with hydriodic acid, forming normal secondary amylic iodide:

$$\underset{\alpha\text{-Amylene.}}{CH_2{=}CH(C_3H_7)^{\alpha}} \;+\; HI \;=\; \underset{\text{Amylic iodide.}}{CH_3.CHI.C_3H_7}.$$

This iodide boils at 146°; its sp. gr. at 0° (32° F.) is 1·537, and at 11° (51°·8 F.) 1·5219; it is only partially decomposed by moist argentic oxide at ordinary temperatures (Wurtz., *Ann. Chem. Pharm.*, cxlviii. 131). α-Amylene unites with bromine, forming a dibromopentane, $C_5H_{10}Br_2$, boiling at about 180° (356° F.).

Amylene from isoprimary amylic iodide. Isopropylethylene (?): $CH_2{=}CH(C_3H_7)^{\beta}$ or $CH_2{=}CH.CH(CH_3)_2$.—According to Flavitzsky (*Ann. Chem. Pharm.*, clxix. 205), the amylic iodide from optically inactive fermentation amylic alcohol, when acted on with an alcoholic solution of potassic hydrate, furnishes an amylene which boils at 25° (77° F.). Most probably the reaction which occurs in this case is that represented by the following equation:

$$\underset{\text{Amylic iodide.}}{CH_2I.CH_2(C_3H_7)^{\beta}} + KHO = KI + OH_2 + \underset{\text{Amylene.}}{CH_2{=}CH(C_3H_7)^{\beta}}.$$

When this amylene is combined with hydriodic acid, and the resulting amylic iodide is decomposed with potassic hydrate, an amylene is obtained, boiling at 35° (95° F.), identical with that formed by the action of dehydrating agents on fermentation amylic alcohol.

Amylene from isoprimary amylic alcohol. (?) *Trimethylethylene:* $C(CH_3)_2{=}CH.CH_3$.—This modification, which is that commonly known as "amylene," is obtained by the action of dehydrating agents on fermentation amylic alcohol. One of the most convenient ways of preparing it is to allow a mixture of 1 pt. of the alcohol with 1½ pts. of zincic chloride, to stand several days with frequent agitation, and then to distil until the thermometer indicates a temperature of 130°—140° (266°—284° F.); or 1 pt. of alcohol may be slowly distilled with 2½ pts. of zincic chloride until ⅝ of the liquid has passed over; the remaining fluid portion is then poured off from the chloride, and the operation repeated 3 or 4 times with fresh quantities of alcohol. The amylene is separated from the distillate by fractional distillation. It is a colourless mobile liquid of sp. gr. ·663 at 0° (32° F.), and boils at about 35° (95° F.).

It was long supposed that this amylene bore a very simple relation to the alcohol from which it is produced, its formation being assumed to take place in the manner indicated by the equation:

$$\underset{\text{Amylic Alcohol.}}{CH_2(OH).CH_2.CH(CH_3)_2} - OH_2 = \underset{\text{Amylene.}}{CH_2{=}CH.CH(CH_3)_2}.$$

Flavitzsky's recent experiments (*loc. cit.*, and *Deut. chem. Ges. Ber.*, 1875, viii. 264), however, clearly show that this is not the case, and tend to prove that the amylene prepared in the manner described has the formula $C(CH_3)_2{=}CH.CH_3$, an isomeric change having taken place during its formation. The occurrence of such change is by no means surprising, for the result of the action of zincic chloride on amylic alcohol is extremely complex: Wurtz found (*Ann. Chem. Pharm.*, cxxviii. 225) that a mixture of hydrocarbons of the paraffin and olefine series was produced under these circumstances, in which he was able to prove the presence of the following members:

Amylene,	Pentane,
Hexylene,	Hexane,
Heptylene,	Heptane,
Octylene,	Octane,
Nonylene,	Nonane,
Decylene or Diamylene,	Decane.

He also obtained evidence that still higher terms of the two series of hydrocarbons were formed.

Amylene combines directly with the haloid acids, with chlorine and bromine, with hypochlorous acid, nitric peroxide, and a number of other compounds. The iodopentane, or amylic iodide, which is formed by its union with hydriodic acid, boils at about 130° (266° F.), but is at the same time partially decomposed; it is readily acted upon by moist argentic oxide, being converted into an amylic alcohol, which appears to be identical with the tertiary alcohol, *ethyldimethylcarbinol* (Flavitzsky):

$$\underset{\text{Amylene.}}{C(CH_3)_2{=}CH.CH_3} + HI = CI(CH_3)_2.CH_2.CH_3;$$

$$2CI(CH_3)_2.CH_2.CH_3 + Ag_2O + OH_2 = \underset{\text{Ethyldimethylcarbinol.}}{2C(OH)(CH_3)_2.CH_2.CH_3} + 2AgI.$$

Amylene is very readily polymerized by sulphuric acid, but by passing a slow stream of carbonic anhydride laden with amylene vapour into a mixture of 2 pts. sulphuric acid and 1 pt. water, a considerable amount of an amylic hydric sulphate is produced (Flavitzsky, *Ann. Chem. Pharm.*, clxv. 157); the alcohol obtained on distilling this compound with water appears to be ethyldimethylcarbinol (see Amylic alcohols, Isopropylcarbinol):

$$\underset{\text{Amylene.}}{C(CH_3)_2{=}CH.CH_3} + H_2SO_4 = C(HSO_4)(CH_3)_2.CH_2.CH_3;$$

$$C(HSO_4)(CH_3)_2.CH_2.CH_3 + OH_2 = \underset{\text{Ethyldimethylcarbinol.}}{C(OH)(CH_3)_2.CH_2.CH_3} + H_2SO_4.$$

Amylene from ethyldimethylcarbinol.—The amylene which is produced by the action of potassic hydrate on the amylic iodide from ethyldimethylcarbinol (Jermolajeff, *Deut. chem. Ges. Ber.*, iv. 560):

$$CI(CH_3)_2.CH_2.CH_3 + KHO = \underset{\text{Amylene.}}{C(CH_3)_2{=}CH.CH_3} + KI + OH_2,$$

appears to be identical with that which is formed by the action of zincic chloride on fermentation amylic alcohol (*ibid.*, viii. 264). It boils at 35° (95° F.), and combines with hydriodic acid, reproducing the iodide from which it was prepared.

Amylene from diethylcarbinol: $CH(CH_3){=}CH(C_2H_5)$. (?) *Methylethylethylene.*—The amylic iodide from diethylcarbinol is converted by potassic hydrate into an amylene, which boils at 36° (96°·8 F.):

$$CH_3.CH_2.CHI.CH_2.CH_3 + KHO = KI + OH_2 + CH_3.CH{=}CH.CH_2.CH_3.$$

It combines with hydriodic acid, forming an iodide, which has the same boiling-point (145° C.) and sp. gr. (1·520 at 0° C.) as that from which it was obtained (Saytzeff a. Wagner, *Ann. Chem. Pharm.*, clxxv. 351).

Amylenes from other sources.—By heating monochlorinated isoprimary amylic chloride with sodium, Buff (*ibid.* cxlviii. 349) obtained an amylene boiling at 28°—30° (82°·4—86° F.), but none of its derivatives were examined.

According to Le Bel (*Compt. Rend.*, lxxv. 267), the oil obtained on distilling the pitch from Pechelbronn in Alsace contains two isomeric amylenes, one of which combines with hydrochloric acid in the cold, forming an amylic chloride boiling at 85°—87° (185°—188°·6 F.), the corresponding iodide boiling at 130° (266° F.), and the alcohol, $C_5H_{11}.OH$, at 105° (221° F.). The second amylene requires to be heated with hydrochloric acid to produce the amylic chloride; this boils at 95° (203° F.), and is converted by potassic iodide into amylic iodide, boiling at 145° (293° F.), from which an amylic alcohol boiling at 120° (248° F.) may be obtained. These two amylenes, therefore, would seem to be identical, the former with β-, and the latter with α-amylene.

(1233) HEXYLENE or HEXENE: $C_6H_{12} = 84$.—Although hydrocarbons of the composition C_6H_{12} have been obtained from a variety of sources (*vid.* Hecht, *Ann. Chem. Pharm.*, clxxii. 62) very little is at present known about the greater number of them.

NORMAL or α-HEXYLENE or HEXENE. *Primary butylethylene*: $CH_2{=}CH.CH_2.CH_2.CH_2.CH_3$, or $CH_2{=}CH(C_4H_9)^{\alpha}$, is formed by the action of an alcoholic solution of potassic hydrate on the secondary hexylic iodide from mannite:

$$CH_3.CHI(C_4H_9)^a + KHO = KI + OH_2 + CH_2{=}CH(C_4H_9)^a.*$$

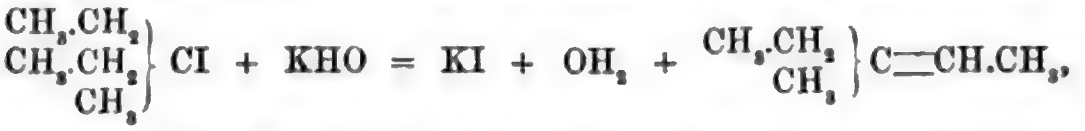
It occurs in the light oils from boghead and Cannel coal, and is amongst the products of the decomposition of paraffin by heat (1164). By acting with potassic acetate on the mixture of chlorohexanes formed by chlorinating normal hexane, Schorlemmer obtained a hexylene boiling at about 70° (158° F.). This, however, would seem to be a mixture of isomeric olefines. The hexylene obtained by Geibel and Buff (*Ann. Chem. Pharm.*, cxlv. 110) on heating dichlorohexane from petroleum hexane with sodium is probably α-hexylene.

α-Hexylene is a colourless liquid, which boils at 65°—66° (149°—150°·8 F.) under the pressure of 710 mm. of mercury; its sp. gr. at 0° (32° F.) is ·6996 (Hecht, *ibid.*, clxv. 150). It unites readily with hydriodic acid, reforming secondary hexylic iodide.

Hexylene from Pinacolic Alcohol. (?) *Tertiary butylethylene:* $CH_2{=}CH.C(CH_3)_3$, or $CH_2{=}CH(C_4H_9)^\delta$.—According to Friedel and Silva (*Compt. Rend.*, lxxvi. 229) the action of potassic hydrate converts the iodide of tertiary butyl-methyl-carbinol or pinacolic alcohol into a hexylene boiling at about 70° (158° F.):

$$CH_3.CHI.(C_4H_9)^\delta + KHO = KI + OH_2 + CH_2{=}CH(C_4H_9)^\delta.$$

Hexylene from diethylmethylcarbinol. (?) *Dimethylethylethylene:* $CH(CH_3){=}C(CH_3)(C_2H_5)$.—This hydrocarbon, produced by the reaction:



$$\left.\begin{matrix}CH_3.CH_2\\CH_3.CH_2\\CH_3\end{matrix}\right\}CI + KHO = KI + OH_2 + \begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\Big\}C{=}CH.CH_3,$$

boils at 68°—72° (154°·4—161°·6 F.); hydriodic acid reconverts it into the iodide from which it is formed (Tschaikowsky, *Deut. chem. Ges. Ber.*, v. 330).

Other Hexylenes.—Hexylenes have been obtained by Prunier (*Compt. Rend.*, lxxvi. 98) by the action of nascent hydrogen on bromopropylene, and by Silva by the action of argentic acetate on monochlorinated diisopropyl; neither of these hydrocarbons has been examined, however.

Pechelbronn petroleum, according to Le Bel, contains two isomeric hexylenes, one of which combines with hydrochloric acid in the cold, and the other on warming, forming hexylic chlorides which boil respectively at about 116° (240°·8 F.) and 123° (253°·4 F.).

(1234) HEPTYLENE or HEPTENE: $C_7H_{14} = 98$.—When the isomeric paraffins, normal heptane, ethyl-isoamyl, and the hydrocarbon boiling at about 90° (194° F.), which is contained, together with normal heptane, in Pennsylvania petroleum, are treated with chlorine, monochlorinated paraffins are produced which on being decomposed with potassic acetate yield heptylenes; in each case, however, the product appears to be a mixture of isomeric olefines (Schorlemmer, *Journ. Chem. Soc.*, 1873, xxvi. 323). Thus, of the heptylene from normal heptane which boils at about 98° (208°·4 F.), somewhat less than one-half combines with cold hydrochloric acid, producing a heptylic chloride which boils with decomposition at about 140° (284° F.); the remaining portion of the hydrocarbon when heated at 120° (248° F.) with hydrochloric acid forms an isomeric heptylic chloride boiling at 147°—150° (300°·2—302° F.). The hydrocarbon from which this latter is produced is probably α- or normal heptylene, $CH_2{=}CH(C_5H_{11})^a$. By far the greater portion of the heptylene boiling at 90°—92° (194°—197°·6 F.), from the isomeric heptane from petroleum, combines readily with cold hydrochloric acid; but only a little more than one-half of the heptylene boiling at about 91° (195°·8 F.) from ethyl-isoamyl combines with this acid in the cold, forming a heptylic chloride boiling at 134°—137° (273°·2—278°·6 F.).

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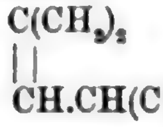
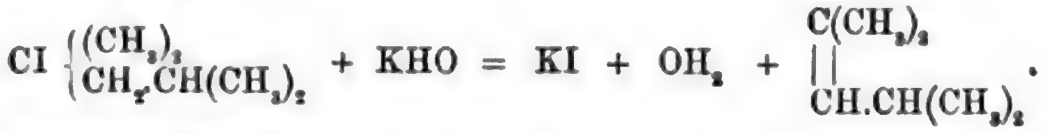
* If, however, the butylene from secondary butylic iodide has the constitution $CH(CH_3){=}CH(CH_3)$, it is very probable that this hexylene is $CH(CH_3){=}CH(C_3H_7)^a$.

Heptylene from dimethylisobutylcarbinol. (?) *Dimethylisopropylethylene:*



$$\begin{array}{l}C(CH_3)_2\\ \|\\ CH.CH(CH_3)_2\end{array}$$

or $C(CH_3)_2{=}CH(C_3H_7)^\beta$.—The iodide of dimethylisobutyl-carbinol, when decomposed by an alcoholic solution of potassic hydrate, yields a heptylene boiling at 83°—84° (181°·4—183°·2 F.) of the sp. gr. ·714 at 0° (32° F.):

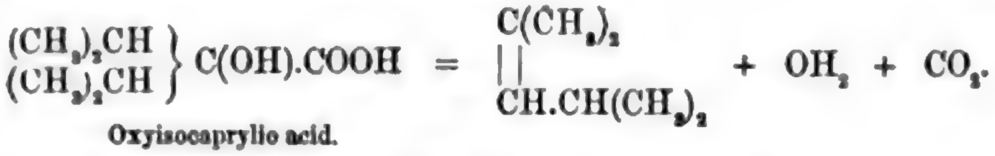


$$CI\left\{\begin{array}{l}(CH_3)_2\\ CH_2.CH(CH_3)_2\end{array}\right. + KHO = KI + OH_2 + \begin{array}{l}C(CH_3)_2\\ \|\\ CH.CH(CH_3)_2\end{array}.$$

Dimethylisobutylic iodide.

This heptylene combines very readily with hydriodic acid, reproducing dimethylisobutylic iodide (Pawlow, *Deut. chem. Ges. Ber.*, vii. 729).

A heptylene which is very probably identical with that from dimethylisobutyl-carbinol was obtained by Markownikoff (*Zeits. Chem.*, 1871, 268) by heating oxyisocaprylic acid with water and a few drops of sulphuric acid to 160° (320° F.):



$$\left.\begin{array}{l}(CH_3)_2CH\\ (CH_3)_2CH\end{array}\right\} C(OH).COOH = \begin{array}{l}C(CH_3)_2\\ \|\\ CH.CH(CH_3)_2\end{array} + OH_2 + CO_2.$$

Oxyisocaprylic acid.

It boils at 81°—83° (177°·8—181°·4 F.), and at 14° (57°·2 F.) has the sp. gr. ·6985.

Heptylene from triethylcarbinol: $C(C_2H_5)_2{=}CH.CH_3$; *or Methyldiethylethylene.*—When triethylcarbinol is heated with an oxidizing mixture of potassic dichromate and sulphuric acid, a small quantity of a heptylene is produced, which, however, has not yet been examined. Its formation is doubtless due to the dehydrating action of the sulphuric acid.

(1235) OCTYLENE or OCTENE: $C_8H_{16} = 112$.—*Normal* or *α-Octylene. Hexylethylene:* $CH_2{=}CH(C_6H_{13})^\alpha$, which is obtained by distilling the normal secondary octylic alcohol, methyl-hexyl-carbinol, with fused zincic chloride:

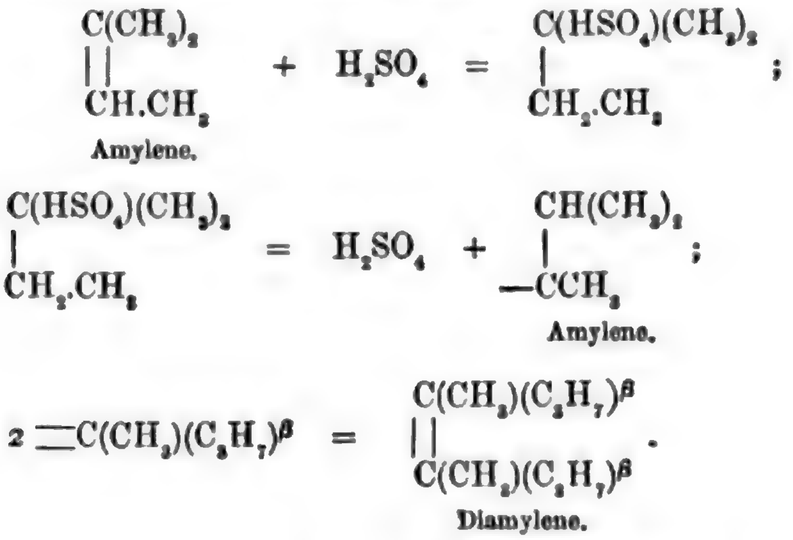
$$\underset{\text{Methylhexylcarbinol.}}{CH_3.CH(OH).C_6H_{13}} = OH_2. + \underset{\text{Octylene.}}{CH_2{=}CH.C_6H_{13}},$$

is the only octylene which has yet received attention. It is a colourless liquid, which boils at 126°—128° (258°·8—262°·4 F.), and at 25° (71°·6 F.) has the sp. gr. ·714 (Neison, *Journ. Chem. Soc.*, 1874, xxvii.). It unites with bromine, forming a dibromoctane, which is decomposed on distillation; with chlorine it produces a dichloroctane, which boils at 205°—210° (401°—410° F.).

(1236) NONYLENE or NONENE: $C_9H_{18} = 126$.—None of the Nonylenes have hitherto been examined.

(1237) DECYLENE or DECENE: $C_{10}H_{20} = 140$.—The only decylene which has been examined is the so-called *Diamylene*, which is formed together with amylene, triamylene, tetramylene, &c., by the action of zincic chloride on fermentation amylic alcohol. It is best prepared, however, by the action of sulphuric acid on amylene. For this purpose, a quantity of amylene not exceeding 50 grammes is introduced into a stoppered glass cylinder placed in ice-cold water, and twice its volume of a well-cooled mixture of 2 vols. concentrated sulphuric acid and 1 vol. water is added. The reaction is at first violent, and much heat is evolved; but as soon as it has moderated, the mixture should be shaken from time to time until no further action is observed; the oily layer floating on the sulphuric acid is then removed, washed with water, dried over calcic chloride, and the diamylene separated by fractional distillation. Diamylene thus prepared boils at 150°—153° (302°—307°·4 F.) under the pressure of 720 mm. of mercury; its sp. gr. at 0° (32° F.) is ·8416, and at 20° (68° F.) ·8248 (Schneider, *Ann. Chem. Pharm.*, clvii. 207).

The conversion of amylene into diamylene by sulphuric acid, and, in fact, the polymerization of the olefines generally under the influence of that reagent, is readily explained, on the supposition that the olefine at first enters into union with the acid, and that the resulting compound is broken up again into sulphuric acid and olefine, two or more molecules of the latter coalescing at the moment of separation to form the polymeric hydrocarbon. If the formula assigned to diamylene by Butlerow (*Ann. Chem. Pharm.*, clxxiii. 375) be adopted, the conversion of amylene into diamylene may be thus represented:

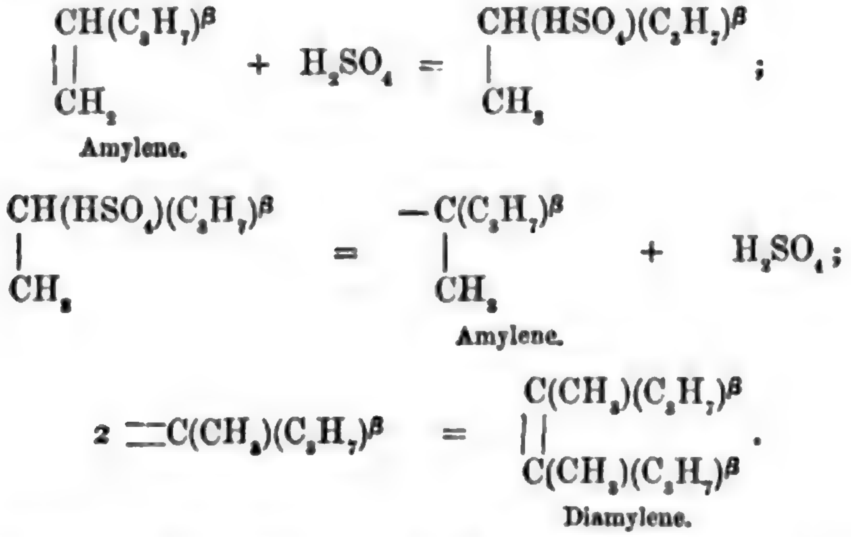


$$\begin{array}{l}\mathrm{C(CH_3)_2}\\ \|\\ \mathrm{CH.CH_3}\\ \text{Amylene.}\end{array} + \mathrm{H_2SO_4} = \begin{array}{l}\mathrm{C(HSO_4)(CH_3)_2}\\ |\\ \mathrm{CH_2.CH_3}\end{array};$$

$$\begin{array}{l}\mathrm{C(HSO_4)(CH_3)_2}\\ |\\ \mathrm{CH_2.CH_3}\end{array} = \mathrm{H_2SO_4} + \begin{array}{l}\mathrm{CH(CH_3)_2}\\ |\\ \mathrm{-CCH_3}\\ \text{Amylene.}\end{array};$$

$$2\,{=}\mathrm{C(CH_3)(C_3H_7)}^{\beta} = \begin{array}{l}\mathrm{C(CH_3)(C_3H_7)}^{\beta}\\ \|\\ \mathrm{C(CH_3)(C_3H_7)}^{\beta}\\ \text{Diamylene.}\end{array}.$$

The amylene, which boils at 25° (77° F.) is also converted into the same diamylene by sulphuric acid:



$$\begin{array}{l}\mathrm{CH(C_3H_7)}^{\beta}\\ \|\\ \mathrm{CH_2}\\ \text{Amylene.}\end{array} + \mathrm{H_2SO_4} = \begin{array}{l}\mathrm{CH(HSO_4)(C_3H_7)}^{\beta}\\ |\\ \mathrm{CH_3}\end{array};$$

$$\begin{array}{l}\mathrm{CH(HSO_4)(C_3H_7)}^{\beta}\\ |\\ \mathrm{CH_3}\end{array} = \begin{array}{l}\mathrm{-C(C_3H_7)}^{\beta}\\ |\\ \mathrm{CH_3}\\ \text{Amylene.}\end{array} + \mathrm{H_2SO_4};$$

$$2\,{=}\mathrm{C(CH_3)(C_3H_7)}^{\beta} = \begin{array}{l}\mathrm{C(CH_3)(C_3H_7)}^{\beta}\\ \|\\ \mathrm{C(CH_3)(C_3H_7)}^{\beta}\\ \text{Diamylene.}\end{array}.$$

Diamylene combines with bromine, forming a *dibromodecane* or *diamylene bromide*, $C_{10}H_{20}Br_2$, which cannot be distilled without decomposition.

(1238) *Other Olefines.*—A number of higher homologues of the olefines have been imperfectly described. Some of these are met with amongst the products of destructive distillation, and others have been prepared artificially; the properties of none of these hydrocarbons, however, have been examined.

An *endecylene*, $C_{11}H_{22}$, is obtained on distilling the bromendecane obtained from methylnonylcarbinol, $CH(CH_3)(C_9H_{19})^{a}\,OH$; it boils at 200° (392° F.). Triamylene and tetramylene are products of the action of sulphuric acid, &c. on amylene from fermentation amylic alcohol; they are oily liquids, which boil at 248° (478°·4 F.) and 390°—400° (734°—752° F.). *Cetene*, $C_{16}H_{32}$, *Cerotene*, $C_{27}H_{54}$, and *Melene*, $C_{30}H_{60}$, are obtained on distilling cetylic, cerylic, and melissic alcohols, which are thereby resolved into the corresponding olefines and water; cetene is a liquid which boils at 275° (527° F.), but cerotene and melene are crystalline bodies which are decomposed on distillation.

Haloid Derivatives of the Olefines.

(1239) At present our knowledge of the haloid derivatives of the olefines is somewhat limited. *Preparation.*—They cannot be produced by the action of the halogens on the olefines, but are obtained by withdrawing the elements of a molecule of hydrochloric, hydrobromic, or hydriodic acid from the chloro-, bromo-, or iodo-derivatives of the paraffins (excepting the mono-derivatives, these furnishing the olefines), which for this purpose are usually heated with an alcoholic solution of potassic hydrate. Thus when α- or β-dichlorethane (ethylenic or ethylidenic chloride) is submitted to the action of potassic hydrate, *monochlorethylene*, or *vinylic chloride* as it is frequently termed, is produced:

$$\underset{\text{α-Dichlorethane.}}{CH_2Cl.CH_2Cl} + KHO = \underset{\text{Monochlorethylene.}}{CH_2{=}CHCl} + KCl + OH_2.$$

$$\underset{\text{β-Dichlorethane.}}{CH_3.CHCl_2} + KHO = \underset{\text{Monochlorethylene.}}{CH_2{=}CHCl} + KCl + OH_2.$$

The chlorethylene thus formed may be combined with chlorine, producing a trichlorethane, $C_2H_3Cl_3$, which furnishes *dichlorethylene*, $C_2H_2Cl_2$, when acted upon by potassic hydrate; and from which in turn tetrachlorethane, $C_2H_2Cl_4$, may be prepared and converted into *trichlorethylene*, C_2HCl_3; and finally the pentachlorethane, C_2HCl_5, procured by combining trichlorethylene with chlorine, may be made to furnish *tetrachlorethylene*, C_2Cl_4. The chlorinated paraffins obtained by directly chlorinating paraffins, in most cases are also available for the preparation of chlorinated olefines; bromo-derivatives of the olefines may also be obtained in a precisely similar manner. Very few iodo-olefines are known.

Haloid derivatives of the olefines are also obtained by combining the hydrocarbons of the C_nH_{2n-2} or acetylene series with the haloid acids and halogens. Thus acetylene unites with chlorine to form a dichlorethylene:

$$\underset{\text{Acetylene.}}{C_2H_2} + Cl_2 = \underset{\text{Dichlorethylene.}}{C_2H_2Cl_2};$$

whilst with hydriodic acid it produces iodethylene:

$$\underset{\text{Acetylene.}}{C_2H_2} + HI = \underset{\text{Iodethylene.}}{C_2H_3I.}$$

Properties of the haloid derivatives of the olefines.—They are capable like the olefines of combining with the halogens in the manner described above, and also with the haloid acids and with hypochlorous acid; probably too, with many other compounds which unite with the olefines.

In connexion with the olefines, attention has been already called to the law which appears to govern the combination of the olefines with other compounds—viz., that the more negative radicle of the compound entering into union with the olefine, attaches itself to the least hydrogenized carbon atom in the olefine. It has yet to be ascertained whether this law obtains throughout the whole series of olefines, and whether it is not more or less dependent upon the conditions of experiment. In the case of the haloid derivatives of the olefines, it is known that the mode of combination with the haloid acids is entirely dependent upon the conditions at the moment of union. Thus, bromethylene combines with hydrobromic acid, producing both α- and β-dibromethane:

$$\underset{\text{Bromethylene.}}{CH_2{=}CHBr} + HBr = \underset{\alpha\text{-Dibromethane.}}{CH_2Br.CH_2Br.}$$

$$\underset{\text{Bromethylene.}}{CH_2{=}CHBr} + HBr = \underset{\beta\text{-Dibromethane.}}{CH_3.CHBr_2.}$$

The former is mainly produced by the action of a very concentrated solution of the acid acting at the ordinary temperature, whilst the latter is chiefly formed by the action of a less concentrated solution at a temperature of 100° (212° F.). (Reboul, *Compt. Rend.*, lxx. 398 a. 853.)

It is an interesting circumstance that the converse appears to hold good in the case of the formation of certain of the haloid derivatives of the olefines from haloid derivatives of the paraffins. Thus the chloro- and bromopropylenes formed by heating β-dichloro- and β-dibromopropane with an alcoholic solution of potassic hydrate, are each mixtures of two isomeric bodies:

$$\underset{\beta\text{-Dichloropropane.}}{CH_3.CHCl.CH_2Cl} + KHO = \underset{\text{Chloropropylene.}}{CH_3.CH{=}CHCl} + KCl + OH_2.$$

$$CH_3.CHCl.CH_2Cl + KHO = CH_3.CCl{=}CH_2 + KCl + OH_2.$$

Like the olefines themselves, the haloid derivatives of the olefines in many cases readily undergo polymerization.

(1240) HALOID DERIVATIVES OF ETHYLENE. MONOCHLORETHYLENE. *Vinylic chloride:* $C_2H_3Cl = H_2C{=}CHCl = 62{\cdot}5$.—This compound is prepared by heating α-dichlorethane or ethylenic chloride, $CH_2Cl.CH_2Cl$, with an alcoholic solution of potassic hydrate; it is also obtained in a similar manner, although less readily, from β-dichlorethane or ethylidenic chloride, $CH_3.CHCl_2$. It is a colourless gas, having an alliaceous odour, and may be condensed by cold to a liquid boiling at − 18° (− 0°·4 F.).

α-Dichlorethane is usually prepared for the above purpose by allowing a current of chlorine and a current of ethylene, both in a moist state, to meet in a large glass globe exposed to diffused daylight. It may also be procured by Limpricht's method of passing ethylene gas through a mixture of manganic peroxide and hydrochloric acid, which is gently heated, and the mixture distilled when the gas ceases to be absorbed; but a far better method is to pass ethylene into antimonic chloride, $SbCl_5$, as long as it is absorbed, or when a large quantity is required, ethylene and chlorine simultaneously into antimonic chloride. The product is then distilled until the distillate no longer yields an oily liquid on the addition of water. The oil obtained by either of these processes is separated from the aqueous liquid and agitated, first with a dilute solution of sodic hydrate, and then successively with small quantities of concentrated sulphuric acid as long as the latter becomes coloured. It is finally rectified. The pure substance is a colourless liquid, which is insoluble in water, but miscible with alcohol and ether in all proportions.

There is reason to believe that α-dichlorethane is produced together with β-dichlorethane by the action of chlorine on monochlorethane or ethylic chloride, since it is obtained as a bye-product in the manufacture of chloral (Krämer, *Deut. chem. Ges. Ber.*, iii. 257).

DICHLORETHYLENE: $C_2H_2Cl_2 = 97$.—α-Trichlorethane or chlorethylenic chloride, is readily converted by the action of potassic hydrate into β-dichlorethylene:

$$CH_2Cl.CHCl_2 + KHO = CH_2{=}CCl_2 + KCl + OH_2.$$

It is a colourless liquid, boiling at 37° (98°·6 F.). (Krämer.) According to Berthelot and Jungfleisch (*Compt. Rend.*, lxix. 542), an isomeric compound, α-dichlorethylene, $CHCl{=}CHCl$, boiling at about 55° (131° F.), is obtained on heating the crystalline compound $C_2H_2SbCl_5$, which is produced by passing acetylene into antimonic chloride: $C_2H_2SbCl_5 = C_2H_2Cl_2 + SbCl_3$ (p. 212).

TRICHLORETHYLENE: $C_2HCl_3 = 131{\cdot}5$.—This body is produced by the action of potassic hydrate on α-tetrachlorethane or dichlorethylenic chloride, and also by the action of nascent hydrogen on tetrachlorethylene. It is a colourless liquid, boiling at about 88° (190°·4 F.).

β-Tri- and β-tetrachlorethane (chlor- and dichlorethylidenic chloride) are decomposed by potassic hydrate far less readily than their isomerides; the resulting compounds (di- and trichlorethylene) have not as yet been examined.

TETRACHLORETHYLENE. *Dichloride of Carbon*: $C_2Cl_4 = 166$.—This compound was first obtained by Faraday, who prepared it by passing the vaponr of hexachlorethane, C_2Cl_6, through a red-hot tube; it is also formed by adding hexachlorethane to a mixture of zinc and dilute sulphuric acid, or by the action of potassic hydrate on pentachlorethane. It is a mobile colourless liquid, which boils at 121° (249°·8 F.), and has a sp. gr. of 1·659 at 0° (32° F.).

(1241) MONOBROMETHYLENE.—*Vinylic bromide*: C_2H_3Br or $H_2C{=}CHBr = 107$.—According to Semenoff (*Jahrb. Chem.*, 1864, 480), this compound is most conveniently prepared by adding an aqueous solution of potassic hydrate to α-dibromethane, and dropping in alcohol until the two layers disappear and a homogeneous mixture is obtained; it is then distilled off at a temperature of 45°—50° (104°—122° F.) and purified by rectification. Bromethylene is a colourless liquid which boils at about 24° (75°·2 F.).

The α-dibromethane or ethylenic bromide, required for the production of bromethylene, may be prepared by passing a current of ethylene through bromine, or by placing bromine and a little water in a large bottle previously filled with ethylene, and then passing in the gas as fast as it is absorbed; combination takes place rapidly if gently agitated, and the temperature rises sensibly. The bromine is quickly decolorized, and an ethereal liquid of pleasant odour is obtained, having a pungent, sweetish taste, and which may be purified like the chlorine compound. α-Dibromethane is a colourless liquid, but solidifies at a low temperature to a crystalline mass, which melts at 9° (48°·2 F.).

DIBROMETHYLENE: $C_2H_2Br_2 = 186$.—Bromethylene readily combines with bromine, forming α-tribromethane, $CH_2Br.CHBr_2$, which is also produced by the action of bromine on bromethane or ethylic bromide, and on α-dibromethane at 180°—200° (356°—392° F.). α-Tribromethane boils constantly at 191° (375°·8 F.), and has the sp. gr. 2·624 at 16° (60°·8 F.); it is violently acted upon by sodic ethylate, yielding a mixture of the two isomeric dibromethylenes, thus:

$$CH_2Br.CHBr_2 + NaOC_2H_5 = CHBr{=}CHBr + NaBr + HOC_2H_5.$$
$$CH_2Br.CHBr_2 + NaOC_2H_5 = CH_2{=}CBr_2 + NaBr + HOC_2H_5.$$

When, however, it is heated with potassic acetate and alcohol to 150° (302° F.), β-dibromethylene, $CH_2{=}CBr_2$, alone is produced.

α-Dibromethylene, $CHBr{=}CHBr$, boils at 157° (314°·6 F.), and at 17°

(62°·6 F.) has the sp. gr. 2·12; β-dibromethylene, CH_2═CBr_2, boils at 91° (195°·8 F.) (Tawildarow, *Ann. Chem. Pharm.*, clxxvi. 22).

TRIBROMETHYLENE: $C_2HBr_3 = 265$.—The statements with regard to this compound and to the tetrabromethanes from which it is derived are somewhat discrepant. According to Sabanejeff, the tetrabromethane obtained by combining bromine with acetylene (p. 213) is a liquid which does not solidify in a freezing mixture, and decomposes on distillation at 190° (374° F.) with evolution of much hydrobromic acid, whereas Beraud obtained a crystalline tetrabromethane, melting at 42° (107°·6 F.), by the action of bromine on acetylene-silver suspended in water, and Lennox obtained a tetrabromethane from *crude* dibromethylene and bromine, which crystallized when cooled (Tawildarow, *loc. cit.*). Burgoin has recently prepared a crystalline tetrabromethane, melting at 54°·5 (130° F.), and boiling at 206° (402°·8 F.), by heating dibromosuccinic acid with bromine to 180° (356° F.), and he has confirmed Sabanejeff's statement that the tetrabromethane from acetylene is liquid (*Compt. Rend.*, lxxix. 953). Supposing the substances obtained by Burgoin and Sabanejeff to be pure compounds, analogy favours the assumption that the former is α-tetrabromethane, $CHBr_2.CHBr_2$, and the latter β-tetrabromethane, $CH_2Br.CBr_3$; but if this be the case, isomeric change must have taken place in the formation of the latter from acetylene.

By heating his tetrabromethane with an alcoholic solution of potassic acetate to 120°—140° (248°—284° F.), Sabanejeff obtained tribromethylene as a liquid, boiling at 162° (323°·6 F.). Reboul had previously found that a crystalline tribromethylene is produced, together with tetrabromethane, when acetylene is acted upon by bromine. Sabanejeff states that the tetrabromethane may be separated from the tribromethylene by distillation with steam, which carries over the former. The tribromethylene which remains, crystallizes from alcohol, in which it is only slightly soluble, in plates melting at 175° (347° F.); on account of its high melting-point and slight volatility, Sabanejeff regards it as a polymeride of the liquid tribromethylene. It will be noticed that the difference between the boiling-points of α-dibromethylene and of the liquid tribromethylene is remarkably small (*Ann. Chem. Pharm.*, clxxviii. 112).

TETRABROMETHYLENE: $C_2Br_4 = 344$.—Lennox obtained this compound by the action of potassic hydrate on pentabromethane; it is a white crystalline body which melts at about 50° (122° F.).

Pentabromethane, C_2HBr_5, may be obtained by combining tribromethylene with bromine (Lennox), by combining bromacetylene, C_2HBr, with bromine (Reboul), and by heating tetrabromethane from acetylene with a molecule of bromine to 165° (329° F.); it crystallizes, according to Burgoin (*Compt. Rend.*, lxxx. 325), in long needles which melt at 56° (132°·8 F.).

Hexabromethane, C_2Br_6, which is formed by heating tetra- or pentabromethane with bromine to 180°, decomposes without fusing when heated to 210° (410° F.) into tetrabromethylene and bromine.

(1242) IODETHYLENE. *Vinylic iodide:* $C_2H_3I = H_2C$═$CHI = 154$.—This body is obtained by the action of an alcoholic solution of potassic hydrate on α-diiodethane. It is necessary to employ a dilute solution, and to allow the first action to take place at a low temperature (Baumann, *Ann. Chem. Pharm.*, clxiii. 320). It is a colourless liquid which boils at about 55° (131° F.). It is also obtained in a similar manner from β-diiodethane (Gustavson).

DIIODETHYLENE: $C_2H_2I_2 = 280$.—Berthelot has prepared this compound by heating acetylene with iodine in a closed flask to 100° (212° F.). It is a crystalline substance, melting at about 70° (158° F.) (*ibid.*, clxxviii. 119).

CHLOROBROMETHYLENE: C_2H_2BrCl = (?) CH_2═$CClBr = 141·5$.—H. Müller (*Chem. Soc. Journ.*, [2] ii. 420) obtained this compound by heating chlorodibromomethane or chlorethylenic bromide (b. p. 162°—164° C.), $C_2H_3ClBr_2$, with an alcoholic solution of potassic cyanide. It boils at 55°—58° (131°—136°·4 F.).

Many of the above compounds are characterized by the readiness with which they spontaneously undergo change into white solid polymeric substances. This has been shown to take place in the case of monochlor-, monobrom-, β-dichlor-, β-dibrom-, and chlorobromethylene. According to Baumann (*Ann. Chem. Pharm.*, clxiii. 308), the presence of alcohol or water has no influence, but the polymerization appears to be in some way more or less dependent upon the action of light, the change being rapidly effected when the substances are exposed to sunlight, and but slowly in diffused daylight. Iodethylene is not polymerized when exposed to sunlight, but iodine is liberated; the addition of iodine to bromethylene, moreover, prevents its polymerization.

The polymerization of bromethylene, and probably therefore of the remaining compounds, is accompanied by a considerable contraction, the sp. gr. of bromethylene being 1·52, according to Regnault, whilst that of the polymeride is 2·075 (Baumann).

The monohaloid derivatives of ethylene are extremely stable compounds, and do not enter into reactions of double decomposition; by the action of an alcoholic solution of potassic hydrate, they yield acetylene.

The polymerides of the haloid derivatives of ethylene are decomposed when heated, becoming carbonized with evolution of the haloid acid. They oppose a much greater resistance to the action of reagents than even the parent compounds, and moreover, do not combine with the halogens; thus the polymerized bromethylene dissolves in bromine, but the original substance is again obtained on the addition of water, alcohol, or an alkali; the polymerized chlorethylene does not even dissolve in bromine (Baumann).

(1243) HALOID DERIVATIVES OF PROPYLENE—MONOCHLORPROPYLENE: $C_3H_5Cl = 76·5$.—The three isomeric modifications of monochloropropylene are known:

		B. P. (Cent.)	Sp. Gr.
α-Chloropropylene or allylic chloride	$CH_2Cl.CH{=}CH_2$	46°	·954 at 0°.
β-Chloropropylene . .	$CH_3.CH{=}CHCl$	?	?
γ-Chloropropylene . .	$CH_3.CCl{=}CH_2$	23°	·931 at 0°.

α-Chloropropylene or allylic chloride: $CH_2Cl.CH{=}CH_2$, is produced by the action of an alcoholic solution of potassic hydrate on α-dichloropropane, and it may be prepared by dropping allylic alcohol into a slight excess of phosphorous chloride, or by heating allylic alcohol with hydrochloric acid in a closed tube. It is also readily obtained by adding a slight excess of finely powdered mercuric chloride to a solution of allylic iodide in an equal volume of alcohol: double decomposition takes place with evolution of much heat, and when the mercuric salt is converted into the red iodide, the mixture is distilled, the distillate mixed with water, and the product, after drying, is fractionally distilled in order to separate the ethylic ether and ethylic allylic ether which are simultaneously formed in small quantity. Allylic chloride is a pungent smelling mobile liquid.

β-Chloropropylene: $CH_3.CH{=}CHCl$, is obtained, together with the γ-compound, by acting on β-dichloropropane or propylenic chloride, but it has not yet been prepared in a pure state.

γ-Chloropropylene: $CH_3.CCl{=}CH_2$, appears to be the sole product of the action of an alcoholic solution of potassic hydrate on δ-dichloropropane or methylchloracetol:

$$CH_3.CCl_2.CH_3 + KHO = CH_3.CCl{=}CH_2 + KCl + OH_2.$$

It is also obtained in considerable quantity as a bye-product in the preparation of methylchloracetol from acetone and phosphoric chloride.

α- and γ-Chloropropylene differ remarkably in their behaviour with various reagents; thus even below 100° (212° F.) the α-compound acts upon sodic ethylate or an alcoholic solution of potassic hydrate, and is converted into ethylic allylic ether:

$$\underset{\substack{\alpha\text{-Chloropropylene}\\ \text{(Allylic chloride).}}}{C_3H_5Cl} + \underset{\substack{\text{Sodic}\\ \text{ethylate.}}}{NaOC_2H_5} = \underset{\substack{\text{Ethylic allylic}\\ \text{ether.}}}{C_3H_5.OC_2H_5} + NaCl,$$

whereas γ-chloropropylene furnishes allylene when heated with sodic ethylate to 120° (248° F.):

$$\underset{\gamma\text{-Chloropropylene.}}{C_3H_5Cl} + NaOC_2H_5 = \underset{\text{Allylene.}}{C_3H_4} + NaCl + HOC_2H_5.$$

By the action of hydriodic acid on allylic chloride, allylic iodide is produced, and this is converted by the further action of the acid into isopropylic iodide, whilst δ-chloropropylene forms an iodochloropropane:

$$CH_3.CCl{=}CH_2 + HI = CH_3.CClI.CH_3.$$

When concentrated sulphuric acid is added to well-cooled γ-chloropropylene, hydrochloric acid is evolved, and on distilling the product with water acetone is obtained, the reactions being:

$$\begin{aligned} CH_3.CCl{=}CH_2 + H_2SO_4 &= HCl + CH_3.C(HSO_4){=}CH_2;\\ CH_3.C(HSO_4){=}CH_2 + H_2SO_4 &= CH_3.C(HSO_4)_2.CH_3;\\ CH_3.C(HSO_4)_2.CH_3 + OH_2 &= CH_3.CO.CH_3 + 2H_2SO_4. \end{aligned}$$

When allylic chloride is similarly treated no gas is evolved, and on afterwards distilling with water, chlorisopropylic alcohol or propylene chlorhydrin is obtained (Oppenheim, *Ann. Chem. Pharm. Supbd.*, vi. 353):

$$\begin{aligned} CH_2Cl.CH{=}CH_2 + H_2SO_4 &= CH_2Cl.CH(HSO_4).CH_3;\\ CH_2Cl.CH(HSO_4).CH_3 + OH_2 &= CH_2Cl.CH(OH).CH_3 + H_2SO_4. \end{aligned}$$

DICHLOROPROPYLENE: $C_3H_4Cl_2 = 111$.—Four isomeric dichloropropylenes are known:

		B. P. (Cent.)	Sp. Gr.
α-Dichloropropylene .	$CH_2Cl.CH{=}CHCl$	106°	1·218 at 25°
β-Dichloropropylene .	$CH_2Cl.CCl{=}CH_2$	94°	1·21 at 20°
γ-Dichloropropylene .	$CH_2{=}CH.CHCl_2$	84°	1·170 at 24·5°
δ-Dichloropropylene .	$CH_3.CCl{=}CHCl$	75°	—

α-Dichloropropylene is obtained by the action of phosphorus oxychloride or phosphoric anhydride on dichlorhydrin:

$$CH_2Cl.CH(OH).CH_2Cl - OH_2 = CH_2Cl.CH{=}CHCl.$$

It is a colourless liquid, of the sp. gr. 1·250 at 0° (32° F.), 1·218 at 25° (77° F.), which combines with bromine, forming a *dibromodichloropropane* boiling at 220°—225° (428°—437° F.), of the sp. gr. 2·19 at 0° (32° F.) and 2·147 at 25° (77° F.), according to Friedel and Silva (*Compt. Rend.*, lxxv. 81). According to Hartenstein (*Journ. pr. Chem.* [2], vii. 295) it has the sp. gr. 1·233 at 17°·5 (63°·5 F.), and the dibromodichloropropane which it furnishes boils at 212° (413°·6 F.) and has the sp. gr. 2·083 at 17°·5 (63°·5 F.). α-Dichloropropylene does not combine with hydrochloric acid at 100° (212° F.)

or 150° (302° F.). When heated to 100° (212° F.) with an alcoholic solution of potassic hydrate it is converted into the compound $C_3H_4Cl.OC_2H_5$, which boils at 120°—125° (248°—257° F.), and at 0° (32° F.) has the sp. gr. 1·021.

β-Dichloropropylene: $CH_2{=}CCl.CH_2Cl$.—The product of the action of potassic hydrate on α-trichloropropane or trichlorhydrin has long been known as Reboul's dichloroglycid, but Friedel and Silva have shown that this is a mixture of β-dichloropropylene with a small quantity of α-dichloropropylene. It is also formed, together with a small quantity of δ-dichloropropylene, on heating γ-trichloropropane with water, and by the action of chlorine in the dark on γ-chloropropylene. It combines with hydrochloric acid at 100°—105° (212°—221° F.), furnishing γ-trichloropropane. It also unites with bromine with greater energy than α-dichloropropylene; the dibromodichloropropane which is formed boils at about 205° (401° F.), and at 0° (32° F.) has the sp. gr. 2·161. β-dichloropropylene is converted by heating to 100° (212° F.) with an alcoholic solution of potassic hydrate into the compound $C_3H_4Cl.OC_2H_5$, boiling at 110° (230° F.), of the sp. gr. 1·011 at 0° (32° F.) (Friedel a. Silva, *Compt Rend.*, lxxiv. 955; lxxv. 81).

When it is mixed with concentrated sulphuric acid, and the mixture is subsequently distilled with water, monochloracetone is produced (Henry, *Deut. chem. Ges. Ber.*, v. 190):

$$\underset{\text{β-Dichloropropylene.}}{CH_2Cl.CCl{=}CH_2} + 2H_2SO_4 = HCl + CH_2Cl.C(HSO_4)_2.CH_3;$$

$$CH_2Cl.C(HSO_4)_2.CH_3 + OH_2 = \underset{\text{Monochloracetone.}}{CH_2Cl.CO.CH_3} + 2H_2SO_4.$$

γ-Dichloropropylene: $CH_2{=}CH.CHCl_2$, is produced by the action of phosphoric chloride on acrylic aldehyde or acrolein (Huebner and Geuther, *Ann. Chem. Pharm.*, cxiv. 36):

$$\underset{\text{Acrolein.}}{CH_2{=}CH.COH} + PCl_5 = \underset{\text{γ-Dichloropropylene.}}{CH_2{=}CH.CHCl_2} + POCl_3.$$

According to Aronstein (*Ibid.*, *Supbd.* iii. 184), the compound $C_3H_4Cl.OC_2H_5$ formed by heating it to 130° (266° F.) with an alcoholic solution of potassic hydrate boils at 115°—120° (239°—248° F.).

δ-Dichloropropylene: $CHCl{=}CCl.CH_3$. — When γ-trichloropropane is heated with water, or with potassic hydrate alone or in alcoholic solution, a mixture of β- and δ-dichloropropylene is obtained, consisting chiefly of the latter when potassic hydrate is employed, but chiefly of β-dichloropropylene when water is employed (Friedel a. Silva). The dibromodichloropropane formed by the union of δ-dichloropropylene with bromine boils at about 190° (374° F.).

The higher chlorinated derivatives of propylene have not hitherto been investigated.

(1244) MONOBROMOPROPYLENE: $C_3H_5Br = 121$.—The only three bromopropylenes which theoretically are possible have been obtained; we are indebted to the French chemist Reboul for most of our knowledge of these bodies (*Compt. Rend.*, lxxiv. 613, 669; lxxvi. 1270; lxxix. 317).

		B. P. (Cent.)	Sp. Gr.
α-Bromopropylene or allylic bromide	$CH_2Br.CH{=}CH_2$	71°	1·436 at 15°
β-Bromopropylene .	$CH_3.CH{=}CHBr$	60°	1·428 at 19°·5
γ-Bromopropylene .	$CH_3.CBr{=}CH_2$	48°	1·364 „

α-Bromopropylene or allylic bromide is produced by the action of phosphorous bromide on allylic alcohol (Tollens).

β-Bromopropylene if formed together with *γ-bromopropylene* when β-dibromopropane or propylenic bromide is decomposed with potassic hydrate solution:

$$\underset{\beta\text{-Dibromopropane.}}{CH_3.CHBr.CH_2Br} + KHO = \underset{\beta\text{-Bromopropylene.}}{CH_3.CH{=}CHBr} + KBr + OH_2;$$

$$\underset{\beta\text{-Dibromopropane.}}{CH_3.CHBr.CH_2Br} + KHO = \underset{\gamma\text{-Bromopropylene.}}{CH_3.CBr{=}CH_2} + KBr + OH_2.$$

γ-Bromopropylene is also formed by treating δ-dibromopropane with an alcoholic solution of potassic hydrate:

$$\underset{\delta\text{-Dibromopropane.}}{CH_3.CBr_2.CH_3} + KHO = \underset{\gamma\text{-Bromopropylene.}}{CH_3.CBr{=}CH_2} + KBr + OH_2.$$

When α-bromopropylene is heated for about twelve minutes to 100° (212° F.) with a *saturated* solution of hydrobromic acid in sealed tubes, it is almost completely converted into α-dibromopropane, $CH_2Br.CH_2.CH_2Br$; if, however, a less concentrated acid be employed, more or less β-dibromopropane, $CH_3.CHBr.CH_2Br$, is also formed.

β-Bromopropylene combines slowly with hydrobromic acid, even at 100° (212° F.), and furnishes a mixture of β- and γ-dibromopropane, $CH_3.CH_2.CHBr_2$, the latter of which boils at 130° (266° F.); with bromine this bromopropylene forms a β-tribromopropane, $CH_3.CHBr.CHBr_2$, which boils at 200° (392° F.), and at 18° (64°·4 F.) has the sp. gr. 2·356.

γ-Bromopropylene combines readily even in the cold with hydrobromic acid, forming δ-dibromopropane only; the γ-tribromopropane, $CH_3.CBr_2.CH_2Br$, which is formed by the union of bromine with γ-bromopropylene, boils at 190° (374° F.).

DIBROMOPROPYLENE: $C_3H_4Br_2$ = 200.—At present only two dibromopropylenes are known with certainty, viz.:

		B. P. (Cent.)
β-Dibromopropylene . .	$CH_2Br.CBr{=}CH_2$	142°
δ-Dibromopropylene . . .	$CH_3.CBr{=}CHBr$	about 120°.

β-Dibromopropylene is formed by the action of potassic hydrate on α-tribromopropane or tribromhydrin; probably, however, the product of this action—the so-called dibromoglycid—contains some α-dibromopropylene. It boils at 142° (287°·6 F.). It readily enters into reaction with potassic acetate, potassic thiocyanate, and argentic nitrate, forming *bromallylic acetate*, $C_2H_3O_2.C_3H_4Br$, *bromallylic thiocyanate*, $C_3H_4Br.CSN$, and *bromallylic nitrate*, $C_3H_4Br.NO_3$ (Henry, *Deut. chem. Ges. Ber.*, v. 191, 452).

δ-Dibromopropylene: $CH_3.CBr{=}CHBr$.—The allylene dibromide which is formed together with allylene tetrabromide by the action of bromine on allylene (p. 218) is probably this compound, and the body first obtained by Cahours by treating bromopropylenic bromide with potassic hydrate doubtless also consists mainly of δ-dibromopropylene. The boiling-point of allylene dibromide, according to Oppenheim, is 127°—131° (260°·6—267°·8 F.), but this is probably too high, owing to the presence of allylene tetrabromide; that observed by Cahours (about 120°, or 248° F.) is perhaps nearer the truth.

Several higher brominated derivatives of propylene have been obtained, but very insufficiently described.

CHLOROBROMOPROPYLENES.—Dichlorallylene, $C_3H_2Cl_2$, from croton-chloral, combines with bromine, forming a dibromodichloropropylene, $C_3H_2Cl_2Br_2$, which is not converted into a propane derivative by heating with bromine, but exchanges hydrogen for bromine. The bromodichlorallylene obtained by treating the dibromodichloropropylene with potassic hydrate furnishes with bromine a crystalline *tribromodichloropropylene*, $C_3HCl_2Br_2$, and this compound also does not combine with bromine, but when heated with it up to 160° (320° F.) during several hours is converted into a *tetrabromodichloropropylene*, $C_3Br_4Cl_2$, which is liquid (Pinner, *Deut. chem. Ges. Ber.*, v. 205).

(1245) IODOPROPYLENE: $C_3H_5I = 168$.—Two of these compounds have been obtained, viz.:

		B. P. Cent.
α-Iodopropylene or allylic iodide	$CH_2I.CH{=}CH_2$	101°
γ-Iodopropylene	$CH_3.CI{=}CH_2$	about 80°.

α-Iodopropylene or Allylic iodide may be obtained pure by carefully mixing 80 pts. of allylic alcohol, 127 pts. of iodine, and 10 pts. red phosphorus; after two days the mixture is distilled, and when one-half has passed over, water is added, and the distillation continued until oily drops cease to pass over with the water; the product is washed, dried, and purified by distillation (Tollens a. Henninger, *Ann. Chem. Pharm.*, clvi. 156). It is also produced by the action of hydriodic acid or of iodide of phosphorus on glycerine, but is always contaminated with isopropylic iodide, whereas the product from allylic alcohol is almost free from that compound.

It is a colourless liquid, having a pungent somewhat alliaceous odour, of the sp. gr. 1·839 at 14° (57°·2 F.). By the action of nascent hydrogen it is readily converted into propylene; the best method of effecting this change is to cover granulated zinc with 90 per cent. of alcohol in an appropriate apparatus, add the allylic iodide, and then pour in concentrated hydrochloric acid; the action at once takes place, and the gas evolved contains only about $\frac{1}{8}$ of its volume of hydrogen (Tollens). Hydriodic acid converts it into propylene, and isopropylic iodide, but the formation of these substances appears to be preceded by that of the compound $C_3H_6I_2$ (Erlenmeyer, *Ann. Chem. Pharm.*, cxxxix. 211), thus:

$$\underset{\text{Iodopropylene.}}{C_3H_5I} + HI = \underset{\text{Diiodopropane.}}{C_3H_6I_2};$$

$$\underset{\text{Diiodopropane.}}{C_3H_6I_2} = \underset{\text{Propylene.}}{C_3H_6} + I_2;$$

$$\underset{\text{Diiodopropane.}}{C_3H_6I_2} + HI = \underset{\text{Iodopropane.}}{C_3H_7I} + I_2.$$

Mercury combines directly with allylic iodide, forming *mercurallylic iodide*, C_3H_5HgI; this crystallizes in white scales which are moderately soluble in acetone and warm carbonic bisulphide. The formation of this substance is much facilitated by the addition of an equal volume of alcohol (Oppenheim, *Deut. chem. Ges. Ber.*, iv. 670). Characteristic of this substance is the extreme readiness with which it is converted into the hydrocarbon, C_6H_{10} (see diallyl).

Allylic iodide readily enters into double decomposition with silver and potassium salts: thus the action of potassic ethylate converts it into allylic ethylic ether, $C_3H_5.O.C_2H_5$.

γ-Iodopropylene is probably the substance which is produced by the action of potassic hydrate on the diiodopropane, $CH_3.CI_2.CH_3$, formed by combining allylene with hydriodic acid (Semenoff, *Jahrb. Chem.*, 1865, 494). It has a strong not unpleasant smell; its sp. gr. at 0° (32° F.) is 1·8346, and at 16° (60°·8 F.), 1·8028.

According to Wurtz, no iodopropylene is formed by the action of an alcoholic solution of potassic hydrate on propylenic iodide, this compound being carbonized and partially converted into isopropylic iodide (*Ann. Chem. Pharm., Sup.*, vi. 353).

DIIODOPROPYLENE: $C_3H_4I_2 = 294$.—By exposing allylene to sunlight during two months, in contact with a solution of iodine in potassic iodide, a liquid (? δ-) diiodopropylene is obtained, which boils at about 198° (388°·4 F.) (Oppenheim, *Jahrb. Chem.*, 1865, 492).

TRIIODOPROPYLENE: $C_3H_3I_3 = 420$.—This compound is produced by agitating allylene silver, C_3H_3Ag, with an ethereal solution of iodine until the colour ceases to disappear; it crystallizes in long white needles, which melt at 64° (147°·2 F.) (Liebermann, *Ann. Chem. Pharm.*, cxxxv. 266).

(1246) HALOID DERIVATIVES OF OTHER OLEFINES.—A number of monohaloid derivatives have been obtained by the action of potassic hydrate on the compounds formed by combining the olefines with the halogens, but with few exceptions little is known of them, and the discovery that crude chloro- and bromopropylene are mixtures of isomeric substances renders it probable that many of the haloid derivatives of higher olefines hitherto regarded as pure, will in a similar manner be found to be mixtures. Very few haloid derivatives of the higher olefines containing more than one atom of halogen have been prepared.

§ III. HYDROCARBONS OF THE C_nH_{2n-2} OR ACETYLNE SERIES.

(1247) Special interest attaches to this series of hydrocarbons not only because its first term acetylene, C_2H_2, is the only known compound of carbon and hydrogen which can be obtained by the direct union of its elements, but also on account of the remarkable properties of this hydrocarbon.

Although a number of the homologues of acetylene have been obtained, our knowledge of most of them is at present extremely limited; they are as follows:

		B. P. (Cent.)
Acetylene	C_2H_2	—
Allylene	C_3H_4	—
Isoallylene or allene		
Crotonylene	C_4H_6	18°—25°
Valerylene	C_5H_8	41°—42°
Propylacetylene		48°—49°
Isopropylacetylene		—
Isoprene		38°
Hexoylene	C_6H_{10}	80°
Diallyl		59°
Amylacetylene	C_7H_{12}	100°
Tetramethylallene		70°
Caprylidene	C_8H_{14}	133°
Tetrahydrometaxylene		—
Decenylene	$C_{10}H_{16}$	165°
Menthene		163°
Rutylene		150°
Nonylacetylene	$C_{11}H_{20}$	210°—215°
Benylene	$C_{15}H_{28}$	225°
Cetenylene	$C_{16}H_{30}$	280°

Hofmann has proposed to distinguish the hydrocarbons of this series by the termination *ine*, into which he suggests the termination *ane* of the corresponding paraffins should be changed; no systematic nomenclature has been generally adopted up to the present time, however.

(1248) ACETYLENE OR ETHINE, C_2H_2 or $HC \equiv CH = 26$.—The establishment of the existence of this hydrocarbon is due to Berthelot, to whom indeed we are very largely indebted for our knowledge of acetylene, but it appears to have been discovered by E. Davy in 1836, when decomposing with water a compound of potassium and carbon formed during the preparation of potassium; he called it *Klumene*. Berthelot has shown that it is formed on passing methane, ethylene, or the vapour of alcohol or ether, besides many other substances, through red-hot tubes, and that it is a constant product of the incomplete combustion of all organic bodies. It is present in coal-gas in small quantity.

To obtain it from its elements, a current of hydrogen is passed through a vessel in which two pieces of hard carbon (gas-coke), forming the terminals of a powerful galvanic battery, are intensely heated by the electric current. Berthelot has ascertained that the combination of carbon and hydrogen does not take place at the temperature produced in a furnace capable of fusing porcelain, or even under the influence of the induction spark.

Acetylene is also produced in many other ways: for example, by the electrolysis of the sodic salt of fumaric or maleic acids (Kekulé):

$$\underset{\text{Sodic }\left\{\begin{smallmatrix}\text{fumarate.}\\ \text{maleate.}\end{smallmatrix}\right.}{C_2H_2(CO_2Na)_2} + 2OH_2 = \underset{\text{Acetylene.}}{C_2H_2} + 2CO_2 + 2NaOH + H_2.$$

By Sawitsch's method, of heating bromethylene with an alcoholic solution of potassic hydrate:

$$C_2H_3Br + KOC_2H_5 = C_2H_2 + KBr + C_2H_5OH.$$

By passing the vapour of α-dichlorethane or ethylenic chloride through a porcelain tube filled with pieces of unslaked lime and heated to redness (v. Wilde, *Deut. chem. Ges. Ber.*, vii. 352):

$$C_2H_4Cl_2 + CaO = C_2H_2 + CaCl_2 + OH_2;$$

this is one of the best methods of preparing acetylene when it is required in quantity. By the action of water on the calcium carbide produced by heating Caron's calcium-zinc alloy to a high temperature with carbon (Wöhler). By passing the vapour of chloroform over ignited copper (Berthelot):

$$2CHCl_3 + 3Cu = C_2H_2 + 3Cu_2Cl_2.$$

By the action of the zinc-copper couple on chloroform, bromoform, and iodoform, dissolved in alcohol; the amount produced is greatest when iodoform, and least when chloroform is used (Gladstone a. Tribe, *Chem. Soc. Journ.*, xxviii. 508). When a mixture of carbonic oxide and methane is passed through a red-hot tube (Odling): $CH_4 + CO = C_2H_2 + OH_2$. By passing sparks from a powerful induction coil through methane:

$$2CH_4 = C_2H_2 + 2H_2.$$

The action of the spark is at first rapid, but diminishes as the volume of hydrogen increases; if, however, the acetylene be absorbed as it is formed, nearly four-fifths of the methane may be ultimately converted into acetylene (Berthelot). The vapours of many organic compounds, especially benzene, yield acetylene when submitted to the action of the induction spark. Acetylene is produced in the incomplete combustion of coal-gas in a Bunsen lamp, when, as is often the case, the flame burns within the tube at the small orifice from which the gas issues before it is mixed with air; the peculiar odour which is then observed being due to the acetylene. By burning a jet of air in an atmosphere of coal-gas, acetylene may be obtained in considerable quantity, and a very useful apparatus for this purpose has been devised by McLeod (*Chem. Soc. Journ.*, 1866, p. 152).

In all these cases the acetylene is more or less contaminated with other substances, but it may readily be purified by causing the mixed gases to pass through a solution of cuprous chloride in ammonia; this solution absorbs acetylene rapidly, and forms with it a flocculent, dark-red, insoluble substance. The liquid is afterwards heated to boiling in order to destroy the compound of ethylene with cuprous chloride, which is formed if ethylene is present, and after cooling, the precipitate is collected on a filter and washed; it is then heated with hydrochloric acid, when pure acetylene is evolved. This solution of cuprous chloride is a very delicate test for acetylene: according to Berthelot, the formation of a distinct red film is observable when a drop is introduced into 50 cc. of a gaseous mixture containing so little as ·0001 per cent. by volume of acetylene. The formation of acetylene in cases of incomplete combustion may also readily be shown if a little of the solution be poured into a tall narrow jar filled with the gas or vapour for combustion—ether or benzene vapour, for example; on setting fire to the mixture, holding the jar in a nearly horizontal position, and causing it to revolve so as to distribute the cuprous solution over the sides of the jar, a considerable deposit of the brownish-red copper compound will be obtained.

Acetylene is a colourless gas, having a peculiar characteristic disagreeable odour; it burns with a very bright smoky flame, and is on this account one of the most valuable illuminating constituents of coal-gas. It is soluble in about its own volume of water at 18° (64°·4 F.), whilst absolute alcohol dissolves nearly 6 volumes of the gas. It has not yet been liquefied either by cold or pressure.

By determining the amount of heat evolved during the combustion of acetylene, and comparing it with the amount evolved on combustion of the same quantities of the elements of which it is composed, Thomsen has shown that a very large amount of heat is *absorbed* in the formation of acetylene from its elements, no less than 55,010 units of heat in the formation of 26 grammes of acetylene (*Deut. chem. Ges. Ber.*, v. 773).

Acetylene is decomposed by the induction spark with separation of carbon, and is also almost wholly resolved into its elements when slowly passed through a porcelain tube heated to bright redness; but when heated in a bent glass tube standing over mercury to the temperature at which glass softens, it is gradually, and if sufficient time be allowed, completely converted, with separation of small quantities of carbon and hydrogen, and formation of small quantities of ethylene and ethane, into a mixture of liquid and solid hydrocarbons. This mixture contains, *a,* a very volatile liquid hydrocarbon; *b, benzene,* C_6H_6, to the extent of nearly half the product; *c, cinnamene,* C_8H_8, to the extent of about one-fifth; *d, naphthalene,* $C_{10}H_8$; *e,* a mixture of highly fluorescent oils, boiling at 250°—340° (482°—644° F.); and *f, retene,* $C_{18}H_{18}$. If, however, a piece of coke, previously ignited and cooled under mercury, be introduced into the bent glass tube, the acetylene is resolved under the same conditions as above, into its elements, scarcely any by-products being obtained, showing that the mode of decomposition is greatly influenced by the presence of foreign bodies (Berthelot).

When submitted to the action of the silent electric discharge, acetylene is completely converted into a brown amorphous solid substance (v. Wilde, *Deut. chem. Ges. Ber.*, vii. 357).

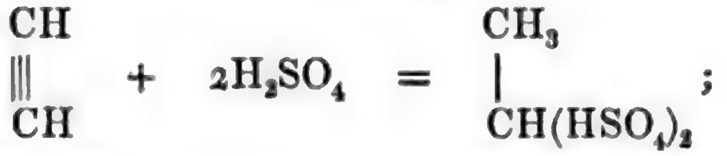
Free hydrogen does not act upon acetylene at ordinary temperatures, but when the gases are heated together, small quantities of ethylene, benzene, naphthalene, and other hydrocarbons are produced. When a mixture of acetylene with twice its volume of hydrogen is placed in contact with platinum-black, the acetylene is rapidly converted into ethane: $C_2H_2 + 2H_2 = C_2H_6$ (v. Wilde). Nascent hydrogen in alkaline liquids readily converts acetylene into ethylene, but this change does not take place in acid liquids (Berthelot). The conversion is best effected by the action of zinc and dilute ammonia solution on the so-called cuprous acetylide; the nascent hydrogen formed by the action of the zinc on the ammonia solution, it may be supposed, produces acetylene, which at the moment of formation combines with the nascent hydrogen, yielding ethylene. The formation of ethylene in this manner from acetylene must be accompanied by the evolution of a very considerable amount of heat, for Thomsen has shown, by determining its heat of combustion, that 10,880 units of heat are absorbed in the formation of 28 grams of ethylene, and since in the production of 26 grams of acetylene 55,010 units of heat are absorbed, the difference between these two numbers—viz., 44,130—represents the number of units of heat evolved in the combination of 26 grams of acetylene with 2 grams of hydrogen.

When a series of powerful induction sparks is passed through a mixture of acetylene with nitrogen, the two gases combine to form hydrocyanic acid (Berthelot). This may readily be shown by passing the sparks between metallic points in a vessel through which a current of nitrogen laden with benzene vapour is transmitted; acetylene is then produced by the action of the spark on the benzene, and combines with the nitrogen; the issuing gas is passed through an alkaline solution, and the presence of the cyanide afterwards demonstrated by the prussian blue test (Perkin).

If mixed with chlorine, acetylene usually explodes spontaneously; this occurs almost immediately, even in diffused light, carbon and hydrochloric acid being formed; sometimes, however, no explosion takes place, but the two gases unite forming *a-dichlorethylene* or *acetylene dichloride*, $C_2H_2Cl_2$. Acetylene is absorbed by antimonic chloride, much heat being evolved; the crystalline compound, $C_2H_2SbCl_5$, which forms, is resolved by heat into a-dichlorethylene, and antimonious chloride, and if heated with antimonic chloride yields *a-tetrachlorethane*, $C_2H_2Cl_4$. When acetylene is passed into bromine covered with a layer of water, and kept cool, *acetylene tetrabromide* or *a-tetrabromethane*, $C_2H_2Br_4$ is produced, together with a small quantity of crystalline tribromethylene. By saturating absolute alcohol with acetylene, and then adding the necessary quantity of bromine to form acetylene dibromide, and, after repeating these operations a sufficient number of times, adding water, an oil is precipitated, consisting of *acetylene dibromide* or *a-dibromethylene* (Sabanejeff, *Ann. Chem. Pharm.*, clxxviii. 113). Acetylene slowly combines with hydrobromic acid, and is converted into *β-dibromethane*, $C_2H_4Br_2$ (Reboul).

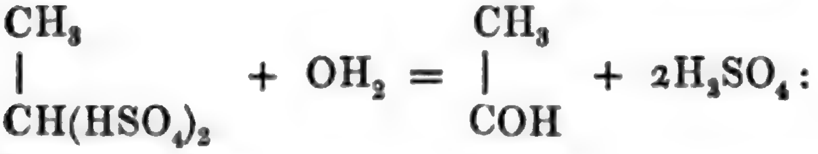
When acetylene is heated with iodine in closed vessels to 100° (212° F.) for about 20 hours, *diiodethylene*, $C_2H_2I_2$, is formed (Berthelot). This compound may be obtained more easily by passing acetylene into a pasty mixture of iodine and alcohol; it crystallizes in long, thin, pliable needles which melt at 73° (163°·4 F.), and possess an intensive characteristic odour; together with this body a very volatile iodide of unknown composition, and a liquid iodide of the same composition as the crystalline acetylene iodide are produced (Sabanejeff, *loc. cit.*). By the action of a concentrated solution of hydriodic acid, acetylene is converted into a mixture of *iodethylene*, C_2H_3I, and *diiodethane*, $C_2H_4I_2$.

According to Berthelot, acetylene is absorbed when briskly agitated for a long time with concentrated sulphuric acid, and converted into *hydric vinylic sulphate*, $C_2H_3HSO_4$; by carefully diluting with water, neutralizing with baric carbonate, and then concentrating the solution, crystalline baric vinylic sulphate is said to be produced. If the acid liquid be distilled with water, a liquid is obtained, slightly more volatile than water, and having a very pungent odour somewhat similar to that of acetone; this Berthelot regards as *vinylic alcohol*, $C_2H_3.OH$. The product, however, does not appear to have been prepared in a pure state, nor to have been analysed, and it is not at all improbable that it is *crotonic aldehyde*, the acetylene being first converted into *acetic aldehyde*, which, under the influence of the acid, furnishes crotonic aldehyde, thus:



$$\begin{array}{c}\mathrm{CH}\\|||\\\mathrm{CH}\end{array} + 2\mathrm{H_2SO_4} = \begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{CH(HSO_4)_2}\end{array};$$

Acetylene. Ethylidenic sulphate.



$$\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{CH(HSO_4)_2}\end{array} + \mathrm{OH_2} = \begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{COH}\end{array} + 2\mathrm{H_2SO_4}:$$

Ethylidenic sulphate. Aldehyde.

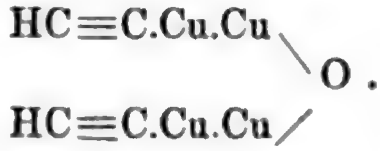
$$\underset{\text{Acetic aldehyde.}}{2C_2H_4O} = \underset{\text{Crotonic aldehyde.}}{C_4H_6O} + OH_2.$$

By the action of potassic permanganate solution at ordinary temperatures acetylene is oxidized to oxalic acid; formic and carbonic acids being formed as secondary products: by a dilute solution of pure chromic acid, it is converted into acetic acid (Berthelot).

(1249) *Metallic derivatives of acetylene.*—When sodium is heated gently in acetylene, the latter is absorbed, and a volume of hydrogen, equal to about half the acetylene, is liberated, *sodium acetylene*, C_2HNa, being formed; at a dull red heat, *disodium acetylene*, C_2Na_2, is produced, and a volume of hydrogen about equal to that of the acetylene is liberated; in both cases small quantities of ethylene and ethane are formed by the union of acetylene with hydrogen. When potassium is melted in acetylene it takes fire, and is converted into *dipotassium acetylene*, C_2K_2. These compounds are immediately decomposed by water, acetylene being regenerated (Berthelot).

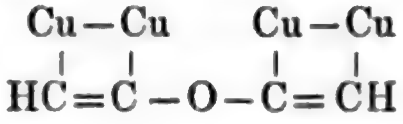
The precipitate of so-called cuprous acetylide (*cuproso-acetylic oxide:* Berthelot; *cuproso-vinylic ether:* Frankland), formed on passing acetylene into an ammoniacal solution of cuprous chloride, after being washed with ammonia until free from chlorine, and then with water, has the composition indicated by the formula $(C_2H_3Cu_2)_2O$ (Berthelot). It is a very unstable compound, detonating by percussion, or when heated to between 95° and 120° (203° and 248° F.). By passing acetylene into a solution of cuprous chloride in potassic chloride and washing the precipitate with potassic chloride solution and afterwards with water, the compound C_2HCu_2Cl (*cuproso-acetylic chloride:* Berthelot) is obtained, which is of a darker colour than the cuprous acetylide. Corresponding silver derivatives $(C_2HAg_2)_2O$ and C_2HAg_2Cl, are formed as white precipitates by passing acetylene into ammoniacal solutions of silver nitrate and chloride: the silver acetylide is a highly explosive compound. Explosive gold and mercury derivatives are also produced on passing acetylene into a solution of sodic auric hyposulphite, or by leaving acetylene for some time in contact with a solution of potassic mercuric iodide, mixed with a little ammonia. Acetylene is reproduced from all these metallic derivatives when they are warmed with hydrochloric acid.

Our knowledge of these substances is very incomplete however, as their examination is extremely difficult on account of their explosive nature; and although Berthelot has assigned formulæ to them, he has not furnished us with the experimental data upon which his conclusions are based. The cuprous derivatives, if the formulæ given to them are correct, may perhaps be represented as follows:



$HC \equiv C.Cu.CuCl.$

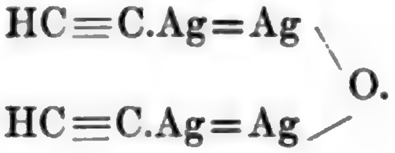
Although cuprous acetylide is frequently regarded as a derivative of vinylic oxide or ether, thus:



$$\begin{array}{ccccccc} Cu & - & Cu & & Cu & - & Cu \\ | & & | & & | & & | \\ HC & = & C & -O- & C & = & CH \end{array};$$

a consideration of the manner in which it is formed, and the fact that acetylene is so readily reproduced on treating it with hydrochloric acid, renders this formula extremely improbable, not to say impossible.

The silver derivatives may be similarly represented if it be admitted that silver is in these compounds trivalent:



$HC \equiv C.Ag = AgCl.$

Carstanjen's formulæ (*Journ. pr. Chem.* [2], iv. 420):

$$(AgC \equiv CAg)_2 + OH_2; \qquad AgC \equiv CAg + HCl;$$

appear less probable, as there is reason to doubt whether both atoms of hydrogen in the acetylene molecule are displaced by silver, since sodium, which appears to have a greater displacing power than silver, furnishes *disodium* acetylene only when heated to dull redness in the gas.

By agitating silver acetylide, suspended in water, with an ethereal solution of iodine, until the latter was no longer decolorized, Berend (*Ann. Chem. Pharm.*, cxxxv. 257) obtained a yellow crystalline compound of the composition $C_4H_2I_4$. The nature of this body is at present unknown, but its formation may, to a certain extent, be regarded as evidence, that, in silver acetylide, the whole of the hydrogen of acetylene is not displaced by silver.

(1250) HOMOLOGUES OF ACETYLENE.—*Preparation:* The only general method at present known of preparing these hydrocarbons, is by the action of an alcoholic solution of potassic hydrate on the monohaloid derivatives of the olefines, thus:

$$C_nH_{2n-1}Br + KO.C_2H_5 = C_nH_{2n-2} + KBr + HO.C_2H_5.$$

It is to be noted, however, that certain of the haloid derivatives of the olefines are not thus acted upon, but are converted by double decomposition into ethers (vide crotonylene):

$$C_nH_{2n-1}Br + KOC_2H_5 = C_nH_{2n-1}.OC_2H_5 + KBr.$$

Properties.—All the hydrocarbons of the series possess characteristic unpleasant odours.

They resemble acetylene in combining in two proportions with the halogens to form either *di*-haloid derivatives of the *olefines*, or *tetra*-haloid derivatives of the *paraffins*:

$$C_nH_{2n-2} + Br_2 = C_nH_{2n-2}Br_2 \; ; \; C_nH_{2n-2} + 2Br_2 = C_nH_{2n-2}Br_4 ;$$

and with the haloid acids forming either *mono*-haloid derivatives of the *olefines*, or *di*-haloid derivatives of the *paraffins*:

$$C_nH_{2n-2} + HI = C_nH_{2n-1}I \; ; \; C_nH_{2n-2} + 2HI = C_nH_{2n}I_2.$$

Several of the homologues of acetylene also furnish characteristic precipitates (metallic derivatives) when added to solutions of cuprous, argentic, gold, mercury, and other salts, from which the original hydrocarbon is reproduced on warming with hydrochloric acid. In no case, however, has the displacement of more than one atom of hydrogen by the metal been observed. The formation of these metallic derivatives appears to be restricted to the hydrocarbons of the form $HC \equiv C.C_nH_{2n+1}$, derived from acetylene by the displacement of one of its hydrogen atoms by a radicle of the C_nH_{2n+1} series.

(1251) *Constitution of the Homologues of Acetylene.*—Although comparatively little is known of the homologues of acetylene, it is already possible to indicate the nature of the various groups of hydrocarbons included in the acetylene series, and it seems especially desirable that this should be done in order to direct attention to the necessity of research in this direction.

Two groups of hydrocarbons, represented by the formulæ:

$$\text{I. } HC \equiv C.C_nH_{2n+1} \quad , \quad \text{II. } C_nH_{2n+1}.C \equiv C.C_nH_{2n+1} ,$$

in which respectively one and both atoms of hydrogen in acetylene are displaced by radicles of the form C_nH_{2n+1}, may be regarded as direct derivatives of acetylene. Hydrocarbons of the first group would seem always to be produced when *aldehydes* of the series $CH_{2n+1}.CH_2.COH$ or *ketones* of the series $C_nH_{2n+1}.CO.CH_3$ are converted into *dichlorinated paraffins* by the action of phosphoric chloride, and these are acted upon with an alcoholic solution of potassic hydrate:

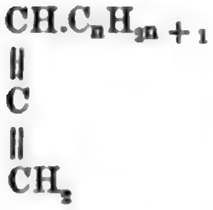
$$\underset{\text{Aldehyde.}}{C_nH_{2n+1}.CH_2.COH} + PCl_5 = \underset{\text{Dichlorinated paraffin.}}{C_nH_{2n+1}.CH_2.CHCl_2} + POCl_3 ;$$

$$\underset{\text{Dichlorinated paraffin.}}{C_nH_{2n+1}.CH_2.CHCl_2} + 2KOH = \underset{\text{Hydrocarbon of acetylene series.}}{C_nH_{2n+1}.C \equiv CH} + 2KCl + 2OH_2.$$

$$\underset{\text{Ketone.}}{C_nH_{2n+1}.CO.CH_3} + PCl_5 = \underset{\text{Dichlorinated paraffin.}}{C_nH_{2n+1}.CCl_2.CH_3} + POCl_3;$$

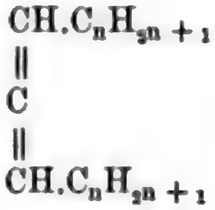
$$\underset{\text{Dichlorinated paraffin.}}{C_nH_{2n+1}.CCl_2.CH_3} + 2KHO = \underset{\text{Hydrocarbon of acetylene series.}}{C_nH_{2n+1}.C{\equiv}CH} + 2KCl + 2OH_2.$$

The remaining groups of the series are constructed on a somewhat different type. The first homologue of acetylene, C_3H_4, exists in two modifications; one of these, known as *allylene*, is the first term of the series $HC{\equiv}C.C_nH_{2n+1}$, being *methylacetylene*, $HC{\equiv}C.CH_3$; the isomeric compound, however, which Henry has proposed to term *allene* (*Deut. chem. Ges. Ber.*, vii. 403), is represented by the formula $H_2C{=}C{=}CH_2$, and from it five groups of hydrocarbons may be derived by the displacement of one, two, three, and four atoms of hydrogen by radicles of the C_nH_{2n+1} series; thus:



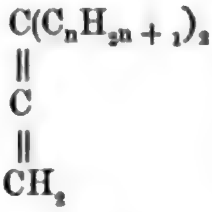
$$\begin{array}{l} CH.C_nH_{2n+1} \\ \| \\ C \\ \| \\ CH_2 \end{array}$$

III.



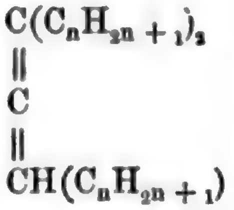
$$\begin{array}{l} CH.C_nH_{2n+1} \\ \| \\ C \\ \| \\ CH.C_nH_{2n+1} \end{array}$$

IV.



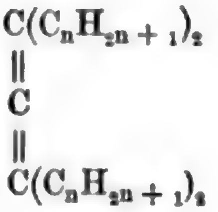
$$\begin{array}{l} C(C_nH_{2n+1})_2 \\ \| \\ C \\ \| \\ CH_2 \end{array}$$

V.



$$\begin{array}{l} C(C_nH_{2n+1})_2 \\ \| \\ C \\ \| \\ CH(C_nH_{2n+1}) \end{array}$$

VI.



$$\begin{array}{l} C(C_nH_{2n+1})_2 \\ \| \\ C \\ \| \\ C(C_nH_{2n+1})_2 \end{array}$$

VII.

It will be noticed that in acetylene and the hydrocarbons derived from it (groups I. and II.), only *two* of the carbon atoms have disposable affinities; thus, for example, when these hydrocarbons combine with chlorine or bromine, the halogen can only attach itself to two carbon atoms, as in the formation of the tetrabromopropane, $CHBr_2.CBr_2.CH_3$, from allylene, $HC{\equiv}C.CH_3$; in the case of allene, however, and of the hydrocarbons derived from it (groups III. to VII.), *three* of the carbon atoms have disposable affinities. Hydrocarbons of the acetylene series, however, may also be formed from some of the monohaloid derivatives of the olefines by the union of the two monad hydrocarbon residues left on the removal of the halogen from two molecules of the haloid derivative; thus:

$$2C_nH_{2n-1}Br - Br_2 = (C_nH_{2n-1})_2 \text{ or } C_{2n}H_{4n-2}.$$

$$\underset{\text{Allylic iodide.}}{2CH_2{=}CH.CH_2I} + 2Na = \underset{\text{Diallyl.}}{CH_2{=}CH.CH_2.CH_2.CH{=}CH_2} + 2NaI.$$

In all such hydrocarbons, *four* of the carbon atoms have disposable affinities. This division will doubtless be found to include a large number of groups of strictly homologous hydrocarbons, although as yet very few of them have been prepared.

(1252) **Allylene or Propene**: C_3H_4 or $HC{\equiv}C.CH_3 = 40$.—This hydrocarbon may be prepared from the crude chloropropylene, C_3H_5Cl, or bromopropylene, C_3H_5Br, obtained from propylenic chloride or bromide, by heating it with sodic ethylate in sealed tubes at 120°, or by passing the vapour through a boiling alcoholic solution of potassic hydrate, or simply by boiling propylenic bromide with an alcoholic solution of potassic hydrate; it is also formed on the electrolysis of potassic citraconate, or mesaconate, $C_3H_4(CO_2K)_2$ (Aarland), and by the action of sodium on the tetrachloropropane $CH_3.CCl_2CHCl_2$ (Fittig a. Pfeffer). It is a colourless gas, having a peculiar alliaceous odour, and produces in an ammoniacal solution of argentic nitrate a white crystalline precipitate of *argentallylene*, C_3H_3Ag; in an ammoniacal solution of cuprous chloride a greenish-yellow precipitate of a cuprous derivative is obtained. Allylene forms with bromine the two compounds $C_3H_4Br_2$ and $C_3H_4Br_4$, both of which are liquid; it unites rapidly with a cold saturated solution of hydrobromic acid, being converted into the bromopropylene $CH_3.CBr{=}CH_2$ (Reboul).

Allylene is readily absorbed by concentrated sulphuric acid; on adding cold water and distilling, a considerable quantity of *acetone* is obtained, and the solution, if neutralized with baric carbonate and concentrated, furnishes a crystalline baric salt of the composition $(C_3H_3SO_3)_2Ba$ (Fittig a. Schrohe, *Deut. chem. Ges. Ber.*, viii. 17 and 367). The formation of acetone doubtless takes place in the following manner:

$$CH_3.C{\equiv}CH + 2H_2SO_4 = CH_3.C(HSO_4)_2.CH_3;$$
$$CH_3.C(HSO_4)_2.CH_3 + OH_2 = CH_3.CO.CH_3 + 2H_2SO_4.$$

At the same time, a portion of the allylene is apparently converted into allylenesulphonic acid: $C_3H_4 + H_2SO_4 = C_3H_3.HSO_3 + OH_2$.

According to Berthelot, allylene is oxidized by potassic permanganate to *malonic acid*, $C_3H_4O_4$, and by chromic acid to *propionic acid*, $C_3H_6O_2$; by-products such as formic, acetic, carbonic and oxalic acids are also obtained; and in the latter case the formation of the acid is, it is said, preceded by that of *allylene oxide* C_3H_6O (? acetone), which boils at 60°—62° (140°—143°·6 F.).

Isoallylene or allene: (?) $CH_2{=}C{=}CH_2$.—When a saturated solution of potassic itaconate, $C_3H_4(CO_2K)_2$, is submitted to electrolysis, this gas is evolved at the positive electrode, together with carbonic anhydride. It is readily distinguished from allylene, since it does not produce a precipitate in an ammoniacal solution of argentic nitrate, being incapable of forming metallic derivatives; it is absorbed by bromine, and converted into the compound $C_3H_4Br_2$, which, when heated with bromine to 100° (212° F.) furnishes a *crystalline* tetrabromopropane, $C_3H_4Br_4$ (Aarland, *Journ pr. Chem.* [2], vi. 256).

(1253) **Crotonylene**: $C_4H_6 = 54$.—Caventou obtained a hydrocarbon of this composition, boiling at about 18° (64°·4 F.), by heating bromobutylene, C_4H_7Br, with sodic ethylate to 100° (212° F.). The butylene bromide, from which the bromobutylene was prepared, was separated by fractional distillation from the mixture of bromides produced by passing into bromine the gases resulting from the decomposition of fermentation amylic alcohol vapour at a red heat. Butlerow has since shown that the so-called isobutylene, $H_2C{=}C(CH_3)_2$, is contained in these gases, but he finds that *pure* bromobutylene prepared from *pure* isobutylene bromide does not yield Caventou's hydrocarbon when heated with sodic ethylate, the action which takes place being represented by the equation:

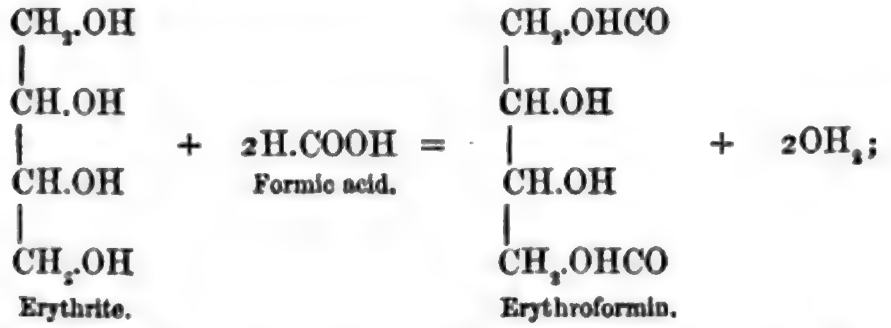
$$C_4H_7Br + NaOC_2H_5 = C_4H_7.OC_2H_5 + NaBr;$$

it therefore follows that the crotonylene in question was derived from some other butylene than isobutylene. (*Zeits. Chem.* [2], vi. 523.)

Crotonylene is formed when a mixture of acetylene and ethylene is passed through a tube heated to dull redness: $C_2H_2 + C_2H_4 = C_4H_6$ (Prunier, *Deut. chem. Ges. Ber.*, vi. 825); it furnishes, with bromine, a crystalline *tetrabromotetrane*, $C_4H_6Br_4$, melting at 113°—115° (235°·4—239° F.). A body apparently identical, and boiling at 20°—25° (66°—77° F.) may be separated by fractional distillation from the hydrocarbons condensed by compression from coal-gas (Caventou, *ibid.* 70). By distilling erythrite with five times its weight of concentrated formic acid, Henninger (*ibid.*) has obtained a crotonylene which furnishes a tetrabromotetrane crystallizing in white needles or glistening rhombic plates, and melting at 116° (240°·8 F.).

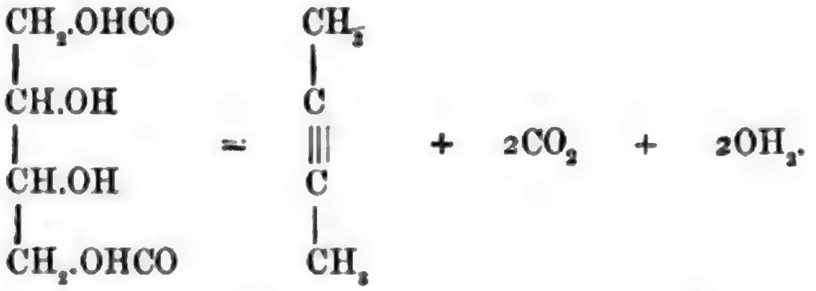
It is not stated that the crotonylene prepared by either of these methods produces a precipitate in solutions of silver or cuprous salt, but a crotonylene which has this property is obtained by the action of potassic hydrate on the dichlorotetrane formed on distilling methyl ethyl ketone, $CH_3.CO.C_2H_5$, with phosphoric chloride (Bruylants, *ibid.* viii. 412). It boils at about 18° (64°·4 F.), and furnishes a crystalline tetrabromotetrane.

It is highly probable that the crotonylene from methyl ethyl ketone is *ethylacetylene*, $HC\equiv C.C_2H_5$; and if the hydrocarbon from the other sources above-mentioned is an isomeric compound, it is doubtless *dimethylacetylene*, $CH_3.C\equiv C.CH_3$. The formation of a crotonylene of the latter kind from erythrite and formic acid is readily explained, the first action consisting in the production of a *formin* or ethereal salt of formic acid, thus:



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \\ \text{Erythrite.} \end{array} + \underset{\text{Formic acid.}}{2H.COOH} = \begin{array}{l} CH_2.OHCO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2.OHCO \\ \text{Erythroformin.} \end{array} + 2OH_2;$$

which subsequently, on distillation, is broken up into crotonylene, carbonic anhydride, and water:



$$\begin{array}{l} CH_2.OHCO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2.OHCO \end{array} = \begin{array}{c} CH_3 \\ | \\ C \\ ||| \\ C \\ | \\ CH_3 \end{array} + 2CO_2 + 2OH_2.$$

(1254) **Propylacetylene. Isopropylacetylene. Valerylene. Isoprene**: $C_5H_8 = 68$.—*Propylacetylene* is produced from methyl propyl ketone, $CH_3.CO.C_3H_7$, by the method already described, and *isopropylacetylene* is similarly prepared from the valeric aldehyde, $(CH_3)_2HC.CH_2.COH$, formed on oxidizing fermentation amylic alcohol. Propylacetylene boils at 48°—49° (118°·4—120°·2 F.). They are mobile colourless liquids, possessing a peculiar alliaceous odour, and produce white precipitates of the composition C_5H_7Ag, in an ammoniacal solution of argentic nitrate, and yellow precipitates in a cuprous solution. They combine with bromine, forming liquid compounds of the composition $C_5H_8Br_2$ and $C_5H_8Br_4$. The dibromamylene thus derived from propylacetylene boils at 190° (374° F.), and that from isopropylacetylene at 175° (347° F.), but the latter is at the same time partially decomposed; the tetrabromopentanes boil at 275° (527° F.), (Bruylants, *Deut. chem. Ges. Ber.*, viii. 406).

Valerylene, which was discovered by Reboul, is obtained by heating amylene bromide, $C_5H_{10}Br_2$, to 140° (284° F.), with a concentrated alcoholic solution of potassic hydrate. It is a mobile liquid of alliaceous odour, which boils at 44° (111°·2 F.); it does not precipitate an ammoniacal cuprous solution; it unites with bromine, forming the compounds $C_5H_8Br_2$ and $C_5H_8Br_4$, of which the former boils at 168°—172° (334°·4—341°·6 F.). Inasmuch as the nature of Reboul's amylene bromide is not known, the composition of valerylene is uncertain, but it is not improbably a *dimethylallene*, $H_2C{=}C{=}C(CH_3)_2$.

Isoprene is a hydrocarbon obtained together with other products by the dry distillation of caoutchouc and gutta-percha; it boils at 37°—38° (98°·6—100°·4 F.). It absorbs oxygen on exposure to the air, and becomes thickened. In this condition it has powerful bleaching properties, and when it is distilled a violent reaction takes place, and the residue suddenly solidifies to a white amorphous mass of the composition $C_{10}H_{16}O$ (Greville Williams).

(1255) HEXOYLENE, DIALLYL: $C_6H_{10} = 82$.—The first of these hydrocarbons is produced by heating bromohexylene, $C_6H_{11}Br$ (from dibromehexane from American petroleum oil) to 140°—160° (284°—320° F.), with an alcoholic solution of potassic hydrate. The hexoylene boils at 80°—85° (176°—185° F.), (Caventou); at 76°—80° (168°—176° F.), (Reboul a. Truchot). It forms liquid substances with bromine of the composition $C_6H_{10}Br_2$, and $C_6H_{10}Br_4$. Schorlemmer has shown that crude benzene contains a hydrocarbon of the composition C_6H_{10} (*Ann. Chem. Pharm.*, cxxxix. 251).

Diallyl: $CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$.—Diallyl is produced in a variety of ways from the allyl compounds, as, for example, by the action of sodium on α-iodopropylene or allylic iodide, C_3H_5I, and on α-trichloro- and α-tribromopropane, but it is best prepared by adding mercurallylic iodide to a solution of potassic cyanide; an action at once takes place in the cold, and on subsequently distilling, the diallyl passes over with the aqueous vapour (Oppenheim, *Deut. chem. Ges. Ber.*, iv. 672):

$$2C_3H_5HgI + 2KCN = C_6H_{10} + Hg(CN)_2 + Hg + 2KI.$$

It is a mobile colourless liquid, having an ethereal pungent odour like that of the radish; it boils at 59° (138°·2 F.), and at 17° (62°·6 F.) has the sp. gr. 0·685.

The behaviour of diallyl with various substances has been very carefully examined. Thus, when combined with bromine, it furnishes a crystalline tetrabromohexane, $C_6H_{10}Br_4$ which melts at 37° (98°·6 F.), and when gently warmed with iodine a corresponding crystalline tetriodohexane, $C_6H_{10}I_4$. On adding nitric peroxide to an ethereal solution of diallyl, crystals of the compound $C_6H_{10}(NO_2)_4$ separate. When diallyl is heated to 100° (212° F.) with a saturated solution of hydrochloric acid, the compounds $C_6H_{11}Cl$ and $C_6H_{12}Cl_2$ are produced, and corresponding iodo-derivatives are formed on heating it with hydriodic acid. On mixing diallyl and concentrated sulphuric acid, a violent reaction takes place, but if this be moderated by adding the acid gradually and with constant agitation to a solution of diallyl in an equal volume of the pure paraffin hydrocarbons boiling at 55°—60° (121°—140° F.) until no further action is observed, and the lower acid layer be then separated and mixed with water, an oil separates which is a mixture of the compound $C_6H_{12}O$ with a number of hydrocarbons polymeric with diallyl of the composition $(C_6H_{10})_n$ (Jekyll, *Chem. News*, xxii. 221).

(1256) AMYLACETYLENE. TETRAMETHYLALLENE: $C_7H_{12} = 96$. — *Amylacetylene* or *œnanthylidene:* $HC\equiv C(C_5H_9)^a$, is obtained by the action of potassic hydrate on the dichloroheptane, $C_7H_{14}Cl_2$, and dibromoheptane, $C_7H_{14}Br_2$, formed from heptylic aldehyde (Rubien, *Ann. Chem. Pharm.*, cxlii. 294; Bruylants, *Deut. chem. Ges. Ber.*, viii. 409). It is a colourless liquid, of alliaceous odour, which, according to Rubien, boils at 106°—108° (222°·8—226°·4 F.), but according to Bruylants, at 100° (212° F.) It produces a white precipitate, $C_7H_{11}Ag$, in an ammoniacal solution of argentic nitrate, and a yellow precipitate in an ammoniacal cuprous solution; with bromine it furnishes the compounds $C_7H_{12}Br_2$ and $C_7H_{12}Br_4$.

Tetramethylallene: $(CH_3)_2C=C=C(CH_3)_2$.—This hydrocarbon is formed by treating the dichloroheptane from diisobutyl ketone, $(CH_3)_2HC.CO.CH(CH_3)_2$, with an alcoholic solution of potassic hydrate (Henry, *Deut. chem. Ges. Ber.*, viii. 400). It is a liquid of unpleasant odour, which boils at about 70° (158° F.); it does not furnish metallic derivatives.

(1257) CAPRYLIDENE. TETRAHYDROMETAXYLENE: $C_8H_{14} = 100$.—Rubien obtained caprylidene by the action of potassic hydrate on the dibromoctane, $C_8H_{11}Br_2$, formed from octylene or caprylene (? from castor-oil octylic alcohol) and bromine. It is a colourless liquid, of faint alliaceous odour, which boils at 134° (272°·7 F.), and combines with bromine to form the two compounds $C_8H_{14}Br_2$ and $C_8H_{14}Br_4$.

Tetrahydrometaxylene.—When camphoric acid, $C_{10}H_{16}O_4$, is decomposed by heating with hydriodic or hydrochloric acid, a mixture of two hydrocarbons of the compositions C_8H_{14}, which boils at 119° (246°·2 F.) is obtained, about half of which consists of tetrahydrometaxylene—a hydrocarbon which may be produced by heating metaxylene, C_8H_{10}, with hydriodic acid and phosphorus. By the action of concentrated nitric acid, tetrahydrometaxylene is converted into trinitrometaxylene, $C_8H_7(NO_2)_3$.

A third isomeric hydrocarbon, boiling at 105° (221° F.), is obtained by distilling the copper salt of camphoric acid (Wreden, *Deut. chem. Ges. Ber.*, v. 608, 764, 1106; vi. 1381).

(1258) DECENYLENE. MENTHENE. RUTYLENE: $C_{10}H_{18} = 138$.—By successively converting petroleum decane, $C_{10}H_{22}$, into chlorodecane, decylene, and dibromodecane, and submitting the last of these compounds to the action of potassic hydrate, Reboul and Truchot obtained a hydrocarbon of the composition $C_{10}H_{18}$, boiling at about 165° (329° F.), to which they gave the name decenylene. With bromine it furnishes the two compounds $C_{10}H_{18}Br_2$, and $C_{10}H_{18}Br_4$.

Rutylene is formed by heating the dibromodecane from diamylene (diamylene bromide) with an alcoholic solution of sodic hydrate (Bauer, *Ann. Chem. Pharm.*, cxxxv. 344). It boils at about 150° (302° F.). When treated with bromine at a low temperature it is converted into the dibromide $C_{10}H_{18}Br_2$, which is an extremely unstable substance, decomposing even at the ordinary atmospheric temperature.

Menthene is a hydrocarbon produced by the action of phosphoric anhydride on menthol or peppermint-camphor, $C_{10}H_{19}.OH$. It is a transparent mobile liquid, which boils at 163° (325°·4 F.), and has an agreeable odour and cooling taste. It combines with bromine in two proportions, forming the compounds $C_{10}H_{18}Br_2$ and $C_{10}H_{18}Br_4$; the former of these, when treated with potassic hydrate, furnishes a hydrocarbon of the composition $C_{10}H_{16}$ (Oppenheim), whilst the latter is resolved by distillation into cymene, $C_{10}H_{14}$, and hydrobromic acid (Wright).

(1259) **Endecenylene**: $C_{11}H_{20} = 152$.—*Nonylacetylene*, $HC{\equiv}C(C_9H_{19})$, the only known modification of this hydrocarbon, is formed by heating the dichlorendecane from methyl nonyl ketone, $CH_3.CO.C_9H_{19}$, with potassic hydrate (Bruylants, *Deut. chem. Ges. Ber.*, viii. 412). It boils at 210°—215° (410°—419° F.), and produces a white precipitate in an ammoniacal solution of a silver salt, and a brownish yellow precipitate with a cuprous salt.

(1260) **Benylene**: $C_{15}H_{28} = 208$.—By the action of bromine at $-17°$ (1°·4 F.) on triamylene, $C_{15}H_{30}$, a triamylenic bromide, $C_{15}H_{30}Br_2$, is obtained, which is converted by heating with argentic acetate into triamylenic acetate, $C_{15}H_{30}(C_2H_3O_2)$; when this compound is decomposed with potassic hydrate, it yields the hydrocarbon benylene, potassic acetate, and water (Bauer, *Ann. Chem. Pharm.*, cxxxvii. 249). It is a viscid colourless liquid, having but a faint odour, and boils at 230°—240° (446°—464° F.); it combines readily with bromine.

(1261) **Cetenylene** or **Cetine**: $C_{16}H_{30} = 222$, may be produced by splitting off two molecules of hydrobromic acid from cetylene bromide, $C_{16}H_{32}Br_2$ (Chydenius, *Ann. Chem. Pharm.*, cxliii. 267). It is a colourless liquid, lighter than water, and boils without decomposition at 280°—285° (536°—545° F.).

§ IV. Hydrocarbons of the C_nH_{2n-4} Series.—Terpenes.

(1262) Our knowledge of this series chiefly extends to the hydrocarbons of the composition $C_{10}H_{16}$. Only two containing fewer atoms of carbon have been described, viz.: *Valylene*, C_5H_6, and *Carpene*, C_9H_{14}, although Pinner formerly stated (*Deut. chem. Ges. Ber.*, viii. 898, 1282) that a gaseous hydrocarbon of the composition C_3H_2, which he called *propargylene*, might be obtained by acting on the dichlorallylene, $C_3H_2Cl_2$, from croton-chloral (see crotonic aldehyde) with sodium, and treating the product with water; it would seem that a hydrocarbon of this composition does not really exist.

The hydrocarbons $C_{10}H_{16}$, which may be conveniently designated by the name of *terpenes*, constitute a large proportion of the greater number of the *essential* or *volatile oils*, as the odoriferous oils* obtained from plants are usually called. The terpenes from natural sources all exhibit to a greater or lesser extent the power of causing the deviation of circularly polarized light either to the right or to the left. Up to the present time a very large number of varieties have been distinguished, chiefly by reason of their behaviour with polarized light, the terpene from one plant being seldom considered as identical with that derived from another. As few of these have been well examined, however, and there is little doubt that many of the terpenes which have been described have been far from pure, it is not improbable that the number of isomerides of the composition $C_{10}H_{16}$ has been much exaggerated, and therefore that when the terpenes from various sources are carefully studied and compared, some, or even many, now regarded as isomeric, will be found to be identical.

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* The oils furnished by various plants may with few exceptions be divided into three classes: I. those which furnish glycerin and acids of the acetic or oleic series when decomposed by treatment with alkalies; II. those which yield an alcohol of the ethylic series and an acid of the acetic series when similarly treated; and III. those which are not affected by treatment with alkalies, and which contain as a more or less essential constituent a hydrocarbon of the composition $C_{10}H_{16}$ or $C_{15}H_{24}$. The first class includes such well-known substances as olive and palm oils, and the oils of this class are usually termed *fixed oils*, because they cannot be distilled unchanged; they are inflammable, nearly or quite odourless, and scarcely soluble in water, although readily dissolved by alcohol and ether; they produce a permanent greasy stain when applied to paper, and when rubbed upon the skin give rise to an unctuous feeling. The oils of the second class are of comparatively rare occurrence, and have as yet only been obtained from certain umbelliferous plants: thus the oils extracted from the

(1263) VALYLENE: $C_5H_6=66$.—Reboul obtained this hydrocarbon by the action of an alcoholic solution of potassic hydrate

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fruits of *Heracleum giganteum*, *H. spondylium*, and *Pastinaca sativa* are mixtures of ethereal salts, which yield hexylic and octylic alcohols, and acetic and butyric acids on treatment with alkalies; these oils have a more or less fruity odour. The oils of the third class, of which common turpentine-oil may be quoted as an example, like the fixed oils, are inflammable, and sparingly soluble in water, although readily soluble in alcohol and ether; but the greasy mark they produce upon paper is only transient, and they feel harsh instead of unctuous when rubbed upon the skin. Since they can be distilled unchanged, or nearly so, and as they constitute the distinctive compound of the plants which yield them, they are termed *volatile* or *essential oils*. Although the boiling-point of these oils lies considerably above 100° (212° F.), they emit at ordinary temperatures minute quantities of an intensely odorous vapour. Besides the hydrocarbons of the composition $C_{10}H_{16}$ or $C_{15}H_{24}$, which are in many cases, although by no means always, the main constituents of these oils, there is invariably present one or more oxygenated compounds; these latter belong to the most varied classes of bodies, although a comparatively simple genetic relation between them and the associated hydrocarbons may be traced in many instances. Many of the oxygenated compounds are solids, being held in solution in the oil, from which they frequently separate in the crystalline state on cooling. These solid constituents of the essential oils were formerly spoken of collectively as *stearoptenes*, the fluid portion of the oil being termed in contradistinction the *elæoptene*.

A few oils which are not included in the above classes have been obtained from plants. Thus the bitter almond contains a substance known as amygdalin, which, under the influence of a ferment present in the seed, is resolved into sugar, hydrocyanic acid, and *bitter almond oil* or *benzoic aldehyde*, C_7H_6O; mustard seed similarly contains a substance known as myrosin, which, when acted upon by a ferment present in the seed, furnishes *mustard oil* or *allylic isothiocyanate*, $C_3H_5.NCS$. The oils from *Tropæolum majus* and the common garden-cress (*Lepidium sativum*), according to Hofmann, consist of *phenylacetonitrile*, $C_6H_5.CH_2CN$, whilst the oil from the water-cress (*Nasturtium officinale*) is *phenylpropionitrile*, $C_6H_5.C_2H_4.CN$. The same chemist has shown that the oil of the spoon-wort (*Cochlearia officinalis*) is a *secondary butylic isothiocyanate*, $C_4H_9.NCS$.

on the compound $C_5H_8Br_2$, formed from valerylene. It is a mobile liquid of an alliaceous odour, which boils at about 50° (122° F.); it produces a yellow precipitate of a cuprous derivative when added to an ammoniacal solution of cuprous chloride, from which the hydrocarbon is regenerated on warming with dilute hydrochloric acid. When bromine is added drop by drop to carefully cooled valylene, a crystalline mass is obtained, saturated with an oil; the crystals consist of $C_5H_6Br_6$, whilst the oil contains the compound $C_5H_6Br_4$, and perhaps also $C_5H_6Br_2$.

(1264) CARPENE: $C_9H_{14}=122$.—This hydrocarbon is produced, together with other bodies, when the calcium salt of podocarpic acid is destructively distilled (Oudemans, *Ann. Chem. Pharm.*, clxx. 252). It is a mobile liquid having an odour which recalls both that of turpentine and that of storax. It boils at about 155° (311° F.). By the action of bromine it is converted into the substitution derivatives $C_9H_{13}Br$. and $C_9H_{12}Br_2$. It rapidly absorbs oxygen from the air, being converted into a resinous amorphous substance, which approximately has the composition $C_{18}H_{28}O_3$; in this respect, more especially, carpene exhibits a very close resemblance to the terpenes.

(1265) ARTIFICIAL TERPENES: $C_{10}H_{16} = 136$. — A hydrocarbon of the composition $C_{10}H_{16}$ has been synthetically produced by the action of an alcoholic solution of potassic hydrate on the compound $C_{10}H_{18}Br_2$ from rutylene (Bauer a. Verson, *Ann. Chem. Pharm.*, cli. 52). The body thus obtained exhibits most of the properties which characterize the natural terpenes, although optically inactive. It is colourless, and has a strong odour, resembling that of turpentine, and when ignited it burns with a luminous smoky flame; it boils at 156°—160° (312°·8—320° F.). When bromine is added to the well-cooled hydrocarbon, combination at first takes place without evolution of hydrobromic acid, but after the addition of the first few drops of bromine the action becomes violent, and much hydrobromic acid is given off. Nitric acid exerts a powerful oxidizing action. It readily absorbs oxygen from the atmosphere, and on this account mainly its preparation in a state of purity is extremely difficult. Bauer and Verson state that by saturating the hydrocarbon with hydrochloric acid gas and then distilling, an almost colourless liquid, boiling at about 180° (356° F.) was obtained, which approximately had the composition corresponding with the formula $(C_{10}H_{16})_2HCl$; but the portion passing over between 180°—200° (356°—392° F.) decomposed with evolution of hydrochloric acid and blackening. Terebene from turpentine oil was at that time (1869) supposed to form a similar compound with hydrochloric acid, and Bauer and Verson were therefore led to regard their hydrocarbon as perhaps identical with terebene; it has since been shown, however, by Riban that "terebene hydrochloride" has the composition $C_{10}H_{17}Cl$, and there can be little doubt that the substance they obtained was impure. Terpenes have also been prepared artificially by polymerizing isoprene, C_5H_8, and by splitting off the elements of water from the oxygenated compounds of the composition $C_{10}H_{18}O$, contained in various essential oils; these will be described later on.

(1266) NATURAL TERPENES.—Hydrocarbons of the composition $C_{10}H_{16}$ have been obtained from plants of the most various kinds, but those which are of the most importance as articles of commerce are derived from the *Coniferæ*. The oleo-resinous juices which exude from the trees of this order are commonly known as *turpentines*, and are solutions of "resins" in hydrocarbons of the composition $C_{10}H_{16}$; by distilling the turpentines, either alone or with water, these hydrocarbons or *turpentine-oils* are separated. There are many varieties of turpentine-oil; but the two most important commercially, are *French turpentine-oil* derived from the French or Bordeaux turpentine of *Pinus maritima*, and the so-called *English turpentine-oil* from the turpentine collected in the United States of America from *Pinus Australis* and *P. tæda*.

The following account of the extraction of turpentine is given by Hanbury and Flückiger (*Pharmacographia*, p. 546):

> In the United States, turpentine is obtained to the largest extent from *Pinus Australis*, of which tree there are vast forests in North and South Carolina, Georgia, and Alabama. But it is in North Carolina that the extraction is principally carried on.
>
> In the winter, *i.e*, from November to March, the negroes in a *Turpentine Orchard*, as the district of forest to be worked is called, are occupied in making in the trunks of the trees cavities which are technically known as *boxes*. For this purpose a long narrow axe is used, and some skill is required to wield it properly. The boxes are made from 6 to 12 inches above the ground, and are shaped like a distended waistcoat pocket, the bottom being about 4 inches below the lower lip, and 8 or 10 below the upper. On a tree of medium size a box should be made to hold a quart. The less the axe approaches the centre of the tree the better, as vitality is the less endangered. From 1 to 4 boxes are made in each tree, a few inches of bark being left between them. The greater number of trees from which turpentine is now obtained are from 12 to 18 inches in diameter and have three boxes each.
>
> The boxes having been made, the bark and a little of the wood immediately beneath it are *hacked*; and from this excoriation, the sap begins to flow about the middle of March, gradually filling the box. Each tree requires to be freshly hacked every 8 or 10 days, a very slight wound above the last being all that is needed. The hacking is carried on year after year, until it reaches to the height of 12 or 15 feet or more, ladders being used. The turpentine, which is called *dip*,

is removed from the boxes by a spoon or ladle of peculiar form, and collected into barrels. The first year's flow of a new tree, having but a small surface to traverse before it reaches the box, is of special goodness and is termed *Virgin dip.* The turpentine which concretes upon the trunk is occasionally scraped off and barrelled by itself, and is known in the market as *scrape*, or by English druggists as *Common Frankincense* or *Gum Thus.*

Although a large amount of turpentine is shipped to the northern ports for distillation, a still larger is distilled in the neighbourhood of the terpentine orchards. Copper stills are used capable of containing 5 to 20 barrels of turpentine. The turpentine is distilled without water, the volatile oil as it flows from the worm being received in the barrel in which it is afterwards sent to market. When all the oil that can be profitably drawn off has been obtained, a spigot is removed from an opening in the bottom of the still and the residual *Rosin*, appearing as a viscid fluid like molasses, is allowed to flow out. Only the first qualities of rosin, as that obtained from *Virgin dip*, are generally considered worth saving, the less pure sorts being simply allowed to run to waste. When it is intended to save the rosin, the latter is drawn off into a vat of water, which separates the chips and other rubbish, and the rosin is then placed in barrels for the market. A North Carolina turpentine orchard will remain productive under ordinary treatment for fifty years.

The collection of turpentine in the departments of the Landes and Gironde in the south-west of France, chiefly in the neighbourhood of Bordeaux, and the tract of country between Bordeaux and Bayonne, is performed in a more rational manner than in America, inasmuch as the plan of making deep cavities in the tree for the purpose of receiving the rosin, is avoided by the simple expedient of placing a suitable vessel beneath the lowest incision, the bark and a very small portion of the underlying wood only being removed. The trees are first tapped when thirty to forty years old, and the collection takes place from February until October. A notch is first made at the foot of the tree about 3 inches broad and 1 inch high, and above this a fresh notch is made about every 8 days. When the tree is notched in this way to the height of about 8 or 9 feet, the opposite side is similarly treated. By the time that the whole of the bark has thus been removed, the old wounds are healed and the tree may be again tapped. The turpentine which concretes upon the stem is termed in France, *Galipot* or *Barras.*

(1267) FRENCH TURPENTINE-OIL. TEREBENTHENE.—Berthelot, who was the first to study thoroughly the chemical behaviour of this hydrocarbon, applied the name terebenthene to the terpene which is the chief constituent of the French oil; his experiments have recently been carefully revised and much extended by Riban, and our knowledge of terebenthene is now far greater than of any of its numerous isomerides.

To obtain pure terebenthene the commercial oil is washed with a solution of an alkaline carbonate to remove the small quantity of acid substances which it contains, and after being dried, is submitted to a long series of fractional distillations. The oil commences to boil at about 150° (302° F.) or even lower, and the boiling-point rises to 160° (320° F.), but the greater portion passes over at about 156° (312°·8 F.); when the various fractions are examined with the polariscope, it is found that the least volatile portions exhibit the least rotatory power, whilst the maximum rotatory power is possessed by the portion boiling at about 156° (312°·8 F.) (Riban, *Ann. Ch. Phys.* [5], vi. 12).

Terebenthene is a colourless mobile liquid of peculiar aromatic odour. The corrected boiling-point of pure terebenthene under the pressure of 760 mm. of mercury is 156° (312°·8 F.). It exerts a lævorotatory action on the polarized ray; the specific rotatory power determined with the aid of Cornu's apparatus illumined with the yellow monochromatic sodium flame at 10° (50° F.) being $[\alpha]_D = -40^\circ \cdot 30$.* Its density at 0° (32° F.) is ·8767.

(1268) *Compounds of Terebenthene with the Haloid Acids.*—Terebenthene and, in fact, all the terpenes combine readily with a single molecule, and some with two molecules, of hydrochloric, hydrobromic, or hydriodic acid, forming bodies which, from their composition, may be regarded respectively as monohaloid derivatives of hydrocarbons of the acetylene series, and dihaloid derivatives of hydrocarbons of the ethylene series.

Terebenthene hydrochlorides, $C_{10}H_{17}Cl$.—When a slow current of hydrochloric acid gas is passed into cooled terebenthene, a mixture of two isomeric compounds of the formula $C_{10}H_{17}Cl$ is produced, one of which is solid and the other liquid; the relative proportions in which they are formed is dependent upon the temperature, the yield of the solid being the greater the lower the temperature. To obtain the solid terebenthene hydrochloride in a pure state, the semi-solid product is submitted to powerful pressure, and the solid residue then crystallized at a low temperature from alcohol or ether. The substance crystallized once from alcohol melts at 118° (244°·4 F.), but the melting point may be raised to 123°—125° (253°·4—257° F.) by several recrystallizations: even this, however, owing to the occurrence of slight decomposition, is not the true fusion-point, which can only be determined by operating in an atmosphere of hydrochloric acid:† it is then found to be 131°—132° (267°·8—269°6 F.) (Riban). Solid terebenthene hydrochloride crystallizes in white needles, and resembles common camphor both in appearance and odour, so that it has been called "artificial camphor": it also sublimes easily at ordinary temperatures. It is insoluble in water. It is optically active, the specific rotatory power being $[\alpha] = -32°·2$.

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* An explanation of the method of determining the "*specific rotatory power*" of optically active substances will be found under Sugar.

† The following is the method of determining the melting points of the terpene hydrochlorides which has been adopted by Riban. The substance, freed from moisture or alcohol by exposure in a desiccator over calcic chloride (sulphuric acid must not be employed because it rapidly absorbs the vapour of the hydrochloride), is introduced into the bend of a U-tube 2 to 3 mm. in diameter, with thin walls, the ends of which are then drawn out into capillary tubes; the one end is connected with a desiccating apparatus attached to an apparatus for evolving hydrochloric acid gas, and the other is also connected with a drying tube in order to prevent the ingress of moist air. The bend of the U-tube is then immersed in a water-bath heated to about 50° (122° F.), and the hydrochloride is sublimed

The liquid isomeride is obtained in a pure state with extreme difficulty, since even after it has been several times cooled in a refrigerating mixture, and separated from the crystals which form, it still contains a notable quantity of the solid isomeride and also a small quantity of the compound formed by the union of two molecules of hydrochloric acid with terebenthene. The only practicable method of removing these appears to be distillation under diminished pressure. Liquid terebenthene hydrochloride has a more powerful lævorotatory action on polarized light than the solid isomeride.

The solid hydrochloride is not decomposed by water at the ordinary temperature, and is only slowly acted upon even at 100° (212° F.); but at 200° (392° F.) it is completely decomposed into hydrochloric acid and terebene, which is an optically inactive isomeride of terebenthene. Small quantities of polymeric hydrocarbons, and of an oxygenated compound (? $C_{10}H_{18}O$) are also produced. The liquid hydrochloride is rapidly decomposed by water at 100° (212° F.), with separation of hydrochloric acid.

Terebenthene dihydrochloride, $C_{10}H_{18}Cl_2$.—This compound is produced when terebenthene is left for some time in contact with a concentrated solution of hydrochloric acid. It crystallizes in rhombic plates, insoluble in water, but easily soluble in boiling alcohol. It is slowly decomposed, however, by boiling with water or alcohol, and quickly by boiling with an alcoholic solution of potassic hydrate, yielding *terpinol*, $(C_{10}H_{17})_2O$. When purified by successive recrystallizations at a low temperature it melts constantly at 49°·5 (121°·1 F.) (Riban). If mixed with a little concentrated solution of ferric chloride and very gently heated, a rose coloration is produced, which soon passes to an intense violet-red, and finally to blue (Riban).

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in a current of hydrochloric acid gas; it is thus obtained condensed in the form of a ring in the ascending branch of the tube. When the sublimation is completed, the bath is removed, and when the tube is cool, the current of gas is stopped and the capillaries are sealed; the U-tube is then immersed in a bath of paraffin or sulphuric acid, which is gradually heated, and the melting point determined in the usual manner.

Terebenthene hydrobromides and hydriodides.—A mixture of a crystalline and a liquid hydrobromide is obtained by the action of hydrobromic acid on turpentine-oil, and a crystalline dihydrobromide, melting at 42° (107°·6 F.), is produced by the action of phosphoric pentabromide. The product of the action of hydriodic acid on turpentine-oil appears to be a mixture of two isomerides, neither of which has been obtained in a solid state. The action of phosphorus iodide on terpin, $C_{10}H_{18}(OH)_2$, furnishes a dihydriodide, crystallizing in colourless hexagonal plates which melt at 48° (118°·4 F.) (Oppenheim). None of these bodies have as yet been prepared from pure terebenthene.

(1269) POLYMERIZATION OF TEREBENTHENE. *Diterebene* or *Colophene:* $C_{20}H_{32}$.—Many substances possess the power of converting terebenthene (and its isomerides) into isomeric or polymeric modifications. Some act even at ordinary temperatures, others only with the aid of heat: again, whilst many produce the change in a very short time, others act slowly and never cause complete transformation. In some cases very small quantities of the reagent are sufficient to produce complete conversion; thus 1 pt. of boric fluoride, which is the most energetic reagent, instantly converts 160 pts. of terebenthene, with great rise of temperature, into polymeric optically inactive hydrocarbons boiling above 300° (572° F.). Sulphuric acid likewise acts in the cold, but less energetically. Weak mineral acids (like boric acid), and several organic acids (acetic, oxalic, tartaric, and citric acid) act upon terebenthene at 100° (212° F.), but the action is very slow, and not complete even after 50 to 60 hours. Zincic chloride at 100° (212° F.) acts somewhat more energetically. Calcic fluoride and chloride, and even the chlorides of the alkali metals, act upon terebenthene but very feebly; the transformation takes place, however, more quickly in presence of these substances than under the influence of heat alone.

The action of sulphuric acid on terebenthene has been studied by Deville, and recently by Riban. The products which are obtained are 7 or 8 per cent. of *cymene*, $C_{10}H_{14}$, which is probably produced by the reaction: $C_{10}H_{16} + H_2SO_4 = C_{10}H_{14} + 2OH_2 + SO_2$; *terebene*, an isomeride of terebenthene; *diterebene* or *colophene*, $C_{20}H_{32}$; and higher polymerides. According to Riban, the hydrocarbon $C_{15}H_{24}$ is *not* produced.

The diterebene may be separated approximately by distillation; it is then heated for some time with sodium in sealed tubes to 200° (392° F.), to remove oxygenated substances, and afterwards fractionally distilled, when it is obtained as a colourless oily liquid boiling at about 320° (608° F.), of the specific gravity 0·943 (Riban). It is not certain, however, that diterebene even when thus prepared is obtained in a pure state, since Riban found that the hydrochloride prepared from it contained only 5·06 per cent. of chlorine instead of 6·11 per cent. as required by the formula $C_{20}H_{33}Cl$.

Tetraterebenthene: $C_{40}H_{64}$.—When antimonious chloride, $SbCl_3$, is added to terebenthene, much heat is evolved and this hydrocarbon is produced. To prepare it, the chloride is carefully added in small quantities at a time until the addition of a fresh quantity causes only a slight evolution of heat; the temperature not being allowed at any time to rise above 50° (122° F.). The product, which consists of diterebene and tetraterebenthene, is thrown into a considerable quantity of cold absolute alcohol, and then treated with hot alcohol, the residue is dissolved in ether, and the solution filtered; the ether is then distilled off, and the residue heated to 240° (464° F.) in vacuo for an hour. 100 pts. of terebenthene yield about 20 pts. of tetraterebenthene, about 20—25 pts. of antimonious chloride being required.

Tetraterebenthene is a transparent, almost colourless, amorphous, brittle substance, resembling colophony in appearance; it is almost insoluble in alcohol, but soluble in ether, carbonic bisulphide, benzene, petroleum, and turpentine-oil.

It is dextrorotatory, $[\alpha]_D = +20°$; its density at 0° (32° F.) is ·977. It is oxidized with extreme facility on exposure to the air, especially when finely divided; thus Riban found that after exposure to the air for 3 months at a temperature of 40°—45° (104°—113° F.), it was converted into an amorphous substance soluble in alcohol, and approximately of the composition $C_{40}H_{64}O_3$, but there was no reason to believe that the oxidation was complete. It forms with hydrochloric acid a *monohydrochloride*, $C_{40}H_{65}Cl$, and a *dihydrochloride*, $C_{40}H_{66}Cl_2$, both of which are amorphous; the former is obtained by the action of dry hydrochloric acid on the finely powdered hydrocarbon, the latter by saturating an ethereal solution of the hydrocarbon with hydrochloric acid. Tetraterebenthene melts below 100° (212° F.), but it does not volatilize below 350° (662° F.). When submitted to distillation it furnishes 1. a *lævorotatory terpene* boiling at about 176° (348°·8 F.), which appears to be in all respects identical with isoterebenthene (1270); 2. *diterebene;* and 3. *viscid* products boiling above the temperature indicated by the mercurial thermometer (Riban *Ann. Ch. Phys.* [5], vi. 42).

(1270) ISOTEREBENTHENE.—When terebenthene is heated in sealed tubes to 300° (572° F.) for two hours, it is converted into an isomeric hydrocarbon of higher boiling-point, having less action on the polarized ray; to obtain it, the crude product is distilled in order to separate polymeric substances, and then carefully fractioned from sodium. Pure isoterebenthene has a strong odour of oil of lemons; it boils at about 175° (347° F.); its density at 0° (32° F.) is ·8586, and its specific rotatory power is $[\alpha]_D = -9°{\cdot}4$. It is more easily oxidized than any of its isomerides, and when exposed to the air in a thin layer, rapidly absorbs oxygen, and in the course of a few hours is converted into a viscid mass (Riban, *ibid.* p. 215).

Isoterebenthene hydrochloride.—When isoterebenthene is saturated with hydrochloric acid gas, it is converted into a *liquid* hydrochloride, $C_{10}H_{17}Cl$, no trace of a crystalline isomeride being produced. The product, when purified by distillation under diminished pressure, boils at about 110° (230° F.), under a pressure of 2 cm. of mercury, suffering but little decomposition; when distilled under the ordinary pressure, it is partially decomposed, but the greater part passes over at about 210° (410° F.).* Its specific rotatory power is $[\alpha]_D = -0°{\cdot}47$, and its specific gravity at 0° (32° F.) ·9927. It is easily decomposed by water at 100° (212° F.), and by the action of an alcoholic solution of potassic hydrate at the same temperature, it is reconverted into isoterebenthene.

Isoterebenthene dihydrochloride.—Isoterebenthene hydrochloride is readily converted into a solid dihydrochloride, which crystallizes in plates melting at 49°·5 (121°·1 F.). To prepare this compound, isoterebenthene, or its hydrochloride, is dissolved in ether, and the solution, after being saturated with hydrochloric acid, is placed in a shallow vessel. In the course of two or three hours, when the ether has evaporated, a solid mass of the dihydrochloride remains, which is readily purified by crystallization from boiling absolute alcohol. Under similar circumstances terebenthene furnishes a liquid product, which is a combination of the mono- and dihydrochloride:* $C_{10}H_{17}Cl + C_{10}H_{18}Cl_2$. Isoterebenthene dihydrochloride furnishes terpinol when boiled with aqueous alcohol to which some hydrochloric acid has been added.

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* According to Berthelot, solid terebenthene hydrochloride boils with decomposition at about 215° (419° F.).

Isoterebenthene is converted into cymene, $C_{10}H_{14}$, by adding carefully to one molecule a molecule of bromine, and distilling the resulting dibromide with solid potassic hydrate (Riban, *Compt. Rend.*, lxxix. 223).

(1271) *Terebene.*—According to Deville, terebenthene is converted by the action of concentrated sulphuric acid into an optically inactive isomeride, *terebene,* boiling at about 160° (320° F.), which combines with hydrochloric acid to form a liquid hydrochloride of the composition $(C_{10}H_{16})_2HCl$. Riban has recently shown, however, that Deville's terebene is a mixture of an optically inactive terpene with cymene, $C_{10}H_{14}$, and that the liquid hydrochloride is a solution of a solid hydrochloride, $C_{10}H_{17}Cl$, in cymene (*Ann. Ch. Phys.* [5], xi. 232).

To prepare pure terebene, terebenthene is carefully mixed with $\frac{1}{20}$th of its weight of concentrated sulphuric acid, the liquid is then left to stand for twenty-four hours, decanted from the sediment, and distilled; the portion which passes over below 250° (482° F.) is washed with sodic hydrate solution and with water, and after drying is again similarly treated. After five to eight treatments, the product is optically inactive, and may then be resolved by long-continued fractional distillation into terebene (b.p. 156° or 312°·8 F.), cymene (b.p. 175° or 347° F.), a small quantity of a camphor-like substance boiling at about 200° (392° F.), colophene, $C_{20}H_{32}$, which boils at about 318° (604°·4 F.), and a mixture of almost solid substances boiling at higher temperatures. By fractioning the portion boiling at

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* Berthelot has shown that a liquid is produced when the solid hydrochloride and dihydrochloride of terebenthene are mixed, and Riban finds that solid terebenthene and isoterebenthene dihydrochlorides form liquid compounds when added to the solid hydrochlorides of terebenthene, terebene, and of the camphenes.

155°—185° (311°—365° F.) from sodium, pure terebene and pure cymene may be obtained (Riban, *loc. cit.*).

Terebene is a mobile, colourless liquid of faint odour, which does not solidify at −27° (−21°·6 F.). It boils at 155°—156° (311°—312°·8 F.), and its density at 0° (32° F.) is 0·877.

Terebene hydrochloride.—When cooled terebene is submitted to the action of a slow current of hydrochloric acid gas it is entirely converted into a crystalline mass of the hydrochloride, $C_{10}H_{17}Cl$. The crystals are easily reducible to a powder, and are thereby distinguished from those of terebenthene hydrochloride, which are soft and waxy. The crystals purified by sublimation in an atmosphere of dry hydrochloric acid gas still contain about 5 per cent. less chlorine than is required by theory (20·57 per cent.), and the loss increases, even when they are kept in a dry atmosphere, until the percentage of chlorine is reduced to 17 or 18. Terebene hydrochloride melts at 125° (257° F.) when the precautions previously described in the case of terebenthene hydrochloride are taken. It is optically inactive. When washed with cold water, it is decomposed with separation of hydrochloric acid and production of a crystalline isomeride of terebenthene, *β-camphene;* by the action of water at 100° (212° F.), or of an alcoholic solution of potassic hydrate, it is reconverted into liquid terebene (Riban). Terebene hydrochloride does *not* furnish a dihydrochloride when its ethereal or alcoholic solution is saturated with hydrochloric acid.

Polymerization of Terebene.—Terebene is not altered by heating to 300° (572° F.) in sealed tubes (Riban), but when it is mixed with concentrated sulphuric acid much heat is evolved, and it is converted into *diterebene* or *colophene,* $C_{20}H_{32}$, a small quantity of cymene being produced at the same time.

(1272) CAMPHENES.—This name was applied by Berthelot to a number of solid terpenes which he obtained by the action of various reagents on the terpene hydrochlorides.

Active Terecamphene.—Berthelot first prepared this substance by heating solid terebenthene hydrochloride with dry soap or an alkaline stearate. According to Riban (*ibid.* p 353), however, it is best prepared by heating the hydrochloride with its own weight of potassic hydrate, and 3 to 4 times its weight of 96 per cent. alcohol, in sealed tubes for 75 hours. The product is rectified, pressed to remove adhering oil, and then submitted to fractional distillation. It is a white solid like camphor, which melts at 45°—47° (113°—116°·6 F.), and boils at 156° (312°·8 F.). Its specific rotatory power varies with the dilution when it is dissolved in alcohol, and is $[\alpha]_D = -53^\circ \cdot 82 - \cdot 03081(e)$, e being the weight of the solvent in 100 parts of solution. It has a higher density in the liquid state than either of its liquid isomerides, being ·8378 at 60° (140° F.), whilst that of terebenthene is ·8270 (Riban).

It combines with hydrochloric acid to form a crystalline hydrochloride, which, when sublimed in an atmosphere of hydrochloric acid, melts at 145° (293° F.). Its specific rotatory power is of an opposite sign to that of the parent hydrocarbon, being $[\alpha]_D = +30^\circ \cdot 25$. It is decomposed by water at ordinary temperatures, although less rapidly than terebene hydrochloride; and when heated with 50 times its weight of water for 90 hours at 100° (212° F.), it is entirely resolved into hydrochloric acid and solid camphene; the rotatory power of the resulting camphene is reduced to $-8^\circ \cdot 5$, however, owing to the modifying action of the hydrochloric acid.

a-Inactive Terecamphene.—This modification is obtained by heating solid terebenthene hydrochloride with twice its weight of pulverized fused potassic acetate for 30 hours to 170° (338° F.) in a long-necked flask. The product is a mixture of terebene with the camphene, from which the latter crystallizes after washing with alkali and water. Except in optical behaviour, it does not in the least differ from the active terecamphene above described (Riban, *ibid.* p. 370).

β-Inactive Terecamphene.—The formation of this body by the action of cold water on terebene hydrochloride has already been mentioned; it is most readily obtained, however, by heating the hydrochloride with 5 times its weight of sodic stearate to 180° (356° F.) for 30 hours; terebene is simultaneously produced in large quantity, but it may be separated from this by the aid of a refrigerating mixture. It possesses properties similar to those of the a-modification, but is apparently less stable, as it is more readily converted at the moment of separation into terebene (Riban). The hydrochlorides of the a- and β- modifications are decomposed by water even more readily than terebene hydrochloride, the camphenes being regenerated.

Borneocamphene.—According to Riban, artificial borneol, $C_{10}H_{17}.OH([\alpha]_D = +2^\circ \cdot 6)$, prepared from camphor by Baubigny's process (*ibid.* [4], xix. 221), is converted by the action of a saturated solution of hydrochloric acid into an inactive hydrochloride, $C_{10}H_{17}Cl$, which, like all the camphene hydrochlorides, melts at 145° (293° F.). This yields part of its hydrochloric acid to cold water, and is rapidly decomposed at 100° (212° F.), although less rapidly than the hydrochlorides of terebene and the active and inactive terecamphenes;[*] borneocamphene, which may be thus produced, is more conveniently prepared, however, by heating the hydrochloride with an excess of an alcoholic solution of potassic hydrate to 180° (356° F.) for 70 hours. It has similar properties to the inactive camphenes (*ibid.* p. 343).

(1273) TERPENE FROM ISOPRENE.—By heating isoprene, C_5H_8, to 280°—290° (536°—554° F.) for ten hours in sealed tubes from which the air is displaced by carbonic anhydride, Bouchardat has obtained an optically inactive terpene, which boils at 176°—181° (348°·8—357°·8 F.) (*Compt. Rend.*, lxxx. 1446). Its density at 0° (32° F.) is ·866. It has a strong lemon-like odour resembling that of isoterebenthene, and like it is rapidly oxidized on exposure to the air. By the action of hydrochloric acid on the ethereal solution of the hydrocarbon, a liquid product is obtained, which is resolved by distillation under diminished pressure into a liquid hydrochloride and a crystalline dihydrochloride; the former boils at about 145° (293° F.) under a pressure of 10 cm. of mercury, and the latter melts at 49°·5. The resemblance which the hydrocarbon from isoprene exhibits to isoterebenthene renders it very probable that the two are identical.

(1274) ENGLISH TURPENTINE-OIL. AUSTRATEREBENTHENE.—Austraterebenthene, according to Berthelot, is the chief constituent of English turpentine-oil. It has the same specific gravity and boiling-point as terebenthene, but its specific rotatory power is of opposite sign, being $[a] = +21°·5$. Austraterebenthene yields with hydrochloric acid a mixture of a solid and a liquid hydrochloride; the specific rotatory power of the former is $[a] = +11°·7$, but in all other respects it appears to be identical with solid terebenthene hydrochloride. The dihydrochloride of austraterebenthene has the same properties as that derived from terebenthene.

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[*] Riban has published an interesting series of observations on the decomposition of the hydrochlorides of terebenthene, terebene, the terecamphenes, and borneocamphene, when heated with the same weight of water (25 pts.) to 100° (212° F.) in sealed tubes for the same length of time (*Compt. Rend.*, lxxx. 1330). In the case of terebenthene hydrochloride, which is decomposed only to a very slight extent, the amount of hydrochloric acid set free represented as a function of the time is expressed by a straight line; but in the case of the hydrochlorides of the terecamphenes and of terebene, which may be almost totally decomposed by 15 hours' heating, the decomposition is represented by logarithmic curves—that is to say, the decomposition is at first extremely rapid, but after a time takes place slowly. The curve for borneocamphene hydrochloride is of precisely the same character, but this compound does not undergo decomposition quite so completely. A similar investigation of the hydrochlorides of the austraterebenthene series, and of the hydrochlorides of terpenes from other sources is much to be desired.

When heated to 250° (482° F.), austraterebenthene is converted into an isomeric hydrocarbon, boiling at 177° (350°·6 F.), which is perhaps identical with isoterebenthene. Like the latter, it has an odour resembling lemon-oil, and is more easily oxidized than the parent hydrocarbon; its specific rotatory power is $[a] = -10$ (Berthelot), that of isoterebenthene being $[\alpha] = -10{\cdot}87$ (Riban). By continued heating, a polymeric hydrocarbon corresponding to, if not identical with, diterebene is produced.

When submitted to the action of sulphuric acid, austraterebenthene furnishes an optically inactive hydrocarbon which appears to be identical with the terebene from terebenthene.

Austracamphenes are obtained from austraterebenthene hydrochloride in the same way as terecamphenes are formed from terebenthene hydrochloride, and resemble the terecamphenes in all their properties excepting their specific rotatory power, which in the case of austracamphene is $[a] = +22°$, that of the solid hydrochloride of austracamphene being $-5°$ (Berthelot).

Austraterebenthene and its derivatives, however, have not been studied in the same careful way as terebenthene and its derivatives, and doubtless many of the statements with regard to them require more or less correction.

(1275) SUBSTITUTION DERIVATIVES OF THE TERPENES.—Scarcely anything is known of the substitution derivatives of the terpenes. By the action of the halogens additive compounds are apparently always produced, which are extremely unstable substances, however. The action is often extremely violent: thus when paper soaked in turpentine-oil is introduced into a vessel filled with chlorine, the turpentine takes fire; bromine acts similarly; and when a considerable quantity of iodine is suddenly brought in contact with turpentine-oil, explosion frequently ensues. The behaviour of the isomeric terpenes differs considerably. When a molecule of bromine is slowly added to the well cooled terpene, combination takes place without evolution of hydrobromic acid, although, on heating the product, hydrobromic acid is given off freely; in the case of the terpene from orange-peel oil, the resulting dibromide after two or three distillations is resolved almost entirely into cymene, $C_{10}H_{14}$, and hydrobromic acid, whereas the dibromide of austraterebenthene yields very little cymene, but is mainly converted into a brominated terpene. Cymene may also be obtained from the terpenes by adding gradually about half their weight of iodine, then cohobating some time, and afterwards distilling (Kekulé; Oppenheim).

The action of chlorine on the solid hydrochloride from turpentine-oil is said to give rise to the formation of the compound $C_{10}H_{13}Cl_5$, which is easily resolved into hydrochloric acid and *tetrachloroterpene*, $C_{10}H_{12}Cl_4$; the latter is crystalline and melts at 110°—115° (230°—239° F.).

The only well-characterized substitution-derivatives are the *nitrosoterpenes* recently obtained by Tilden. When nitrosyl chloride gas, NOCl, is passed into English turpentine-oil cooled to −10° (14° F.) the gas is freely absorbed and a considerable quantity of a white precipitate is thrown down, the greater part of which disappears, however, if the temperature is allowed to rise. To secure it, therefore, it is necessary to filter it off as quickly as possible, and to stir it up with strong spirit of wine so as to remove the mother liquor without delay. The substance thus obtained forms a snow-white crystalline powder; it has the composition $C_{10}H_{16}$ NOCl. When this body is submitted to the action of an alcoholic solution of sodic hydrate it is converted into an optically inactive nitrosoterpene, $C_{10}H_{15}NO$, which crystallizes from alcohol in transparent rhombic prisms, and melts at 129°—130° (264°·2—266° F.) (Tilden, *Journ. Chem. Soc.* [2], xiii. 514). Isomeric bodies have been obtained from the terpenes of orange-peel oil and lemon oil, but terebene does not furnish a nitroso-compound; the nitrosoterpene from orange oil crystallizes in rhombic plates and melts at 71° (159°·8 F.), whilst that from lemon oil forms long prisms (*private communication*).

(1276) COMPOUNDS OF THE TERPENES WITH WATER.—*Terpin*, $C_{10}H_{18}(OH)_2$.—When turpentine-oil mixed with water is allowed to stand, crystals are frequently deposited, the production of which is favoured by the presence of an acid. These crystals are a hydrate of terpin, $C_{10}H_{18}(OH)_2 + OH_2$; to prepare them in quantity, 8 vols. turpentine-oil are mixed with 2 vols. nitric acid and 1 to 6 vols. alcohol, and the mixture is frequently shaken during the first few days, then left to itself in shallow vessels for several weeks. The crystals which form are pressed, and purified by crystallization from boiling water, with addition of animal charcoal. Terpin hydrate, $C_{10}H_{18}(OH)_2 + OH_2$, as thus prepared, crystallizes in large rhombic prisms; when heated to 100° (212° F.), it melts and is converted into *terpin*, $C_{10}H_{18}(OH)_2$. The same change takes place when the crystals are exposed over sulphuric acid. Terpin melts at 103° (217°·4 F.), and crystallizes on cooling; it sublimes at about 150° (302° F.) in slender needles.

Terpentine hydrate, $C_{10}H_{17}(OH)$.—This compound is sometimes obtained in the preparation of terpin hydrate from turpentine-oil either together with it, or forming the only product. It is a liquid boiling at 200°—220° (392°—428° F.).

Similar hydrates have been obtained from terpenes from other sources than the turpentine-oils; it does not appear, however, that all terpenes are capable of yielding them.

(1277) BEHAVIOUR OF THE TERPENES ON OXIDATION.—Reference has already been made to the fact that turpentine-oil, and, indeed, the terpenes generally, absorb oxygen on exposure to the air, becoming thicker and ultimately resinous; in this gradual oxidation small quantities of acetic, formic, and carbonic acids are produced. It is also generally supposed that part of the atmospheric oxygen is converted into ozone, and that turpentine-oil after prolonged exposure to the air always contains ozone in solution. In a recent paper, however (*Journ. Chem. Soc.* [2], xii. 511; xiii. 210), Kingzett altogether disputes the formation of ozone under these circumstances. According to his experiments, neither ozone nor hydric peroxide is produced, but a small amount of a substance is formed which he regards as a *camphoric peroxide*, $C_{10}H_{14}O_4$; and he believes that when the oxidized oil is shaken with water, this peroxide is converted into hydric peroxide and an acid having the composition of camphoric acid. If the oxidation occur in presence of water, which, however, is by no means essential to the change, this acid and hydric peroxide are found in the aqueous solution at the close of the experiment. Kingzett finds that hydric peroxide is also developed in the oxidation of the terpenes from orange-peel, nutmeg, and wormwood oils under similar circumstances (*Chem. News*, vol. xxxii. p. 138).

According to Sobrero (*Ann. Chem. Pharm.*, 1851, lxxx. 106), when turpentine-oil containing water is exposed for some time to the sun's rays in a large flask filled with oxygen, stellate groups of crystals are deposited on the sides of the vessel, which have the composition $C_{10}H_{18}O_2 = C_{10}H_{16} + O + OH_2$.

Berthelot has shown that by the atmospheric oxidation of the camphenes from terebenthene and austraterebenthene in contact with platinum-black, or by the action of chromic acid or potassic permanganate, substances of the same composition as ordinary camphor, $C_{10}H_{16}O$, are formed, but the quantity obtained was too small to enable him to decide whether the products were identical or isomeric with camphor. Riban, however, has recently succeeded in obtaining considerable quantities of a camphor by oxidizing the lævorotatory camphene from terebenthene (1272) with potassic dichromate and sulphuric acid mixture (*Ann. Ch. Phys.* [5], vi. 386). The product resembles ordinary camphor in appearance, and melts at 172° (341°·6 F.), but it exerts a lævorotatory action on polarized light; $[a]_D = -13^\circ{\cdot}7$.

According to Hempel (*Deut. chem. Ges. Ber.*, viii. 357), when turpentine-oil is oxidized with potassic dichromate and sulphuric acid it is converted into monobasic *terpenylic acid*, $C_8H_{12}O_4$.

Concentrated nitric acid acts very violently on turpentine-oil, often setting it on fire. When the oil is heated with moderately strong nitric acid, resinous substances of unknown composition are produced, which on continued heating gradually dissolve, and finally *terebic acid*, $C_7H_{10}O_4$, is obtained, together with terephthalic acid, $C_6H_4(COOH)_2$, and paratoluic acid, $C_6H_4(CH_3)(COOH)$ (Williams, *loc. cit.* vi. 1094; Hempel, viii. 20). Berthelot states that when turpentine-oil is oxidized with potassic permanganate, a resinous acid, easily soluble in water, is produced.

The behaviour of other terpenes on oxidation has been but little studied. From Wright's observations it appears that the hydrocarbons from nutmeg and orange-peel oils, when oxidized with potassic dichromate and sulphuric acid, furnish small quantities of compounds of the formula $C_{10}H_{16}O$, together with acetic, formic, and carbonic acids, whilst hesperidene from orange-peel, when treated with nitric acid, gives a resinous substance, together with an acid of the formula $C_{10}H_{26}O_{17}$ (*hesperisic acid*), but no toluic or terephthalic acid. Myristicene from nutmeg-oil also furnishes a resin and an acid of the formula $C_{29}H_{26}O_{16}$ (*myristisic acid*) (*Journ. Chem. Soc.* [2], xi. 549).

(1278) TERPENES FROM OTHER SOURCES.—It has already been pointed out that a large number of the oils derived from various plants contain terpenes, so that it will be convenient to give a short description here of the better known of these.

The production of the "essential-oils" containing terpenes is not limited to any particular portion of the vegetable organism. In some natural families, the *Umbelliferæ* for instance, the oil is most abundantly contained in the seeds. The *Aurantiaceæ* yield two different kinds of oil, one of which is obtained from the flower, the other from the rind of the fruit. In the *Myrtaceæ* and *Labiatæ* it exists in the leaves, whilst the *Rosaceæ* contain it only in the petals of the flower.

The oils exist ready formed in the plant, enclosed frequently in special oil-cells, which are often visible to the naked eye, as in the leaves of the *Myrtaceæ* and the peel of the *Aurantiaceæ*.

The oils of lemon and orange are extracted by simple pressure from the rind of the fruit; but the general process of extraction consists in placing appropriate portions of the plant in a still with water, and applying heat. In order to prevent the materials from being over-heated by resting against the sides of the still, which would give to the distillate a disagreeable odour and often spoil the product for perfumers' purposes, it is customary to suspend them in a net or on a perforated metallic vessel in the upper part of the still. A better method of obtaining the oil is to allow steam to pass over the plant, and to condense the vapour afterwards in the usual way. The presence of steam favours the volatilization of the oils at a comparatively low temperature, for it mechanically carries over the vapour; the distillate is at first milky, but the greater portion of the oil separates on standing. The water which is condensed in the receiver along with the oil acquires its odour and taste; such waters constitute the fragrant *distilled waters* of the apothecary.

TERPENES FROM THE CONIFERÆ.—In addition to French and English turpentine, several other varieties are known, derived from coniferous plants. They are as follows:—

Venetian or Larch Turpentine.—This is obtained from *Pinus Larix* L. (*Larix Europæa*), and is chiefly collected in the Tyrol. It is a thick honey-like fluid, and contains about 15 per cent. of a terpene which boils at about 157° (314°·6 F.); this terpene exhibits a feeble lævorotatory action, and readily furnishes a crystalline hydrochloride (Hanbury and Flückiger).

Strasburg Turpentine.—The *Pinus Picea* L. (*Abies pectinata*) or Silver Fir, which grows in the mountainous parts of Middle and Southern Europe, appears to furnish two terpenes. The turpentine extracted from the stem yields a terpene which boils at 163° (325°·4 F.), and exhibits feeble lævorotatory action; but the terpene distilled from the *cones* of the same tree exhibits a very powerful lævorotatory action (Hanbury and Flückiger).

Canada Balsam.—This turpentine is extracted from the *Pinus Balsamea*, or Balsam, or Balm of Gilead Fir, which grows in profusion in the northern and western portion of the United States of America, in Nova Scotia, and in Canada. The greater part of the terpene which it furnishes on distillation with water boils at about 167° (322°·6 F.), and exhibits feeble lævorotatory action (Hanbury and Flückiger).

The resins, which are the main constituents of all the varieties of turpentine, have been very inefficiently studied, excepting that derived from American turpentine. Ordinary resin, or colophony, from American turpentine, and the resins of Pinus Abies and Pinus Larix consist (according to Maly) of the so-called *Abietic anhydride*, $C_{44}H_{62}O_4$. This substance, or closely related bodies, appears also to be contained in the resins of other conifers. Hanbury and Flückiger consider that the resin of Canada balsam is a mixture of two bodies, since they found that only about 78 per cent. of a specimen which they examined was soluble in boiling alcohol, whilst ordinary colophonium dissolves entirely; the remainder was an amorphous mass readily soluble in ether. When colophony is boiled with alkaline solutions, greasy salts of *abietic acid* are formed, the so-called *resin soaps*.

Oil of Juniper. Oil of Savine.—Juniper (*Juniperus communis*) berries furnish, on distillation with water, a small amount of an oil, which is a mixture of a terpene boiling at 155° (311° F.) with a second hydrocarbon of the formula $C_{15}H_{24}$. Both are lævorotatory. The allied conifer, *Juniperus Sabina*, yields a dextrorotatory terpene (Hanbury and Flückiger).

TERPENES FROM AURANTIACEÆ.—*Oil of orange-peel*, which is extracted from the rind of the scarcely ripe fruit of the Sweet or Portugal Orange, consists to the extent of fully 95 per cent. of a terpene, called by Gladstone ***hesperidene***, and of an oxygenated oil of the composition $C_{10}H_{16}O$. The corrected boiling-point of pure hesperidene is 178° (352°·4 F.); the oxygenated oil is contained in the portion boiling at 210°—230° (410°—446° F.), but it is gradually polymerized by heating, and converted into a resin which cannot be distilled (Wright, *Journ. Chem. Soc.* [2], xi. 549). Hesperidene exhibits a powerful dextrorotatory action, and when saturated with hydrochloric acid, is converted into a crystalline dihydrochloride.

Oil of Lemons.—This oil, which is also obtained from the rind of the unripe fruit, appears to consist chiefly of a mixture of two dextrorotatory terpenes, together with a small proportion of an oxygenated oil not yet examined. The crude terpene boils at 170°—180° (338°—356° F.), and has a powerful dextrorotatory action; it readily furnishes a crystalline dihydrochloride, and a crystalline hydrate similar to that of terebenthene.

Oil of Bergamot.—This oil is obtained from the full grown, but still unripe and more or less green fruits of the *Citrus Bergamia*, which is cultivated at Reggio, in Calabria. It is dextrorotatory and boils at from 183°—195° (361°·4—383° F.). It appears to be a mixture of one or more terpenes with a solid substance, the composition of which has not been satisfactorily ascertained. The oil readily furnishes a crystalline hydrate on treatment with nitric acid and water.

Oil of Neroli is the oil prepared by distilling the fresh flowers of the Bigarade or Bitter Orange with water, and is manufactured chiefly in the South of France. Like oil of bergamot, it exhibits a slight dextrorotatory action; and consists apparently of a terpene or terpenes and a solid oxygenated substance. On distillation, the greater part passes over at 185°—195° (365°—383° F.).

Oil of Petit Grain is produced by the distillation of the leaves and shoots either of the Bigarade or Bitter Orange, or of the Portugal or Sweet Orange; it consists of a dextrorotatory terpene boiling at about 173° (343°·4 F.), and an oxygenated oil.

TERPENES FROM MYRISTICEÆ.—*Oil of Nutmeg* has been recently examined by Wright (*loc. cit.*), who finds that it consists chiefly of a terpene boiling at about 164° (327°·2 F.); together with an isomeric terpene boiling at about 176° (348°·8 F.); cymene, $C_{10}H_{14}$; and an oxygenated oil, ***myristicol***, $C_{10}H_{16}O$, which boils at 212°—218° (413°·6—424°·4 F.), but is converted by repeated distillation into resinous non-volatile polymerides. Neither of the terpenes were obtained free from cymene, however; and it is therefore improbable that the boiling-points above given are those of the pure terpenes; at least in the case of that contained in the 164° fraction, the true boiling-point is probably lower. The nutmeg terpenes are dextrorotatory.

Oil of Mace.—The nutmeg is enclosed when fresh in a fleshy net-like envelope, somewhat resembling the husk of a filbert, which when separated and dried constitutes the mace of commerce. Mace oil is said to consist chiefly of a terpene boiling at about 160° (320° F.), together with an oxygenated oil.

TERPENES FROM LAURACEÆ.—*Camphor-oil. Borneene.*—Camphor-oil is the oil which drains out of the crude camphor extracted from the *Laurus Camphora.* Wright found a specimen he examined to consist chiefly of camphor dissolved in a terpene boiling at about 170° (338° F.); it appears also to contain oxygenated oils of the composition $C_{10}H_{14}O$ and $C_{10}H_{18}O$.

Bornean or Sumatran Camphor oil, which is obtained by tapping the *Dryobalanops Camphora*, also chiefly consists of a terpene (*borneene*), boiling at about 165° (329° F.), holding in solution borneol and resin.

By distilling Borneol or Borneo Camphor, $C_{10}H_{18}O$, with phosphoric anhydride, a terpene also known as borneene is obtained, which boils at 173°—178° (343°·4—352°·4 F.).

Oils of Cinnamon and Cassia.—The former of these oils is obtained from the bark of Ceylon cinnamon (*Cinnamomum Zeylanicum*), the latter from Chinese cinnamon. Both consist essentially of *cinnamic aldehyde*, C_9H_8O, together with a variable proportion of hydrocarbons, probably terpenes. The oil obtained in Ceylon by distilling cinnamon leaves consists according to Stenhouse of a terpene, boiling at 160°—165° (320°—329° F.), and *eugenol*, $C_{10}H_{12}O_2$, or $C_6H_3(C_3H_5)\left\{\begin{array}{l}OH.\\OCH_3.\end{array}\right.$

Sassafras oil.—This oil is distilled from the wood of the roots and the root-bark of *Sassafras officinale*, a tree growing in North America. It contains about $\frac{9}{10}$ths of its weight of *safrol*, $C_{10}H_{10}O_2$, and also a dextrorotatory terpene boiling at about 156° (312°·8 F.). A very small quantity of a substance soluble in alkali (? a phenol) is likewise present (Rouette and Grimaux, *Compt. Rend.*, lxvii. 928). Safrol is a colourless oil boiling at 230°—233° (446°—451°·4 F.), which it is said does not solidify at − 20° (− 4° F.); it is converted by bromine into a crystalline pentabromo-derivative, $C_{10}H_5Br_5O_2$. The attempts to ascertain the constitution of safrol have been hitherto unsuccessful, as it is resinized by the action of all ordinary reagents, and even melting potassic hydrate attacks it with difficulty; it appears probable, however, that it is related to eugenol, since it differs very little from it in composition, and both occur in plants of the same order. Oil of sassafras is also said to deposit crystals of sassafras camphor, $C_{10}H_{10}O_2$, when cooled in a refrigerating mixture.

Oil of Bay.—According to Gladstone, the oil from the berries of *Laurus nobilis* is a mixture of a lævorotatory terpene, boiling at 171° (339°·8 F.), and eugenol.

TERPENES FROM UMBELLIFERÆ.—*Oil of Caraway*, distilled from the seeds of *Carum Carvi*, consists, to the extent of about one-third, of a dextrorotatory terpene (*carvene*), boiling at 173° (343°·4 F.), and of *carvol*, $C_{10}H_{14}O$.

Oil of Dill, from the seed of *Anethum graveolens*, also consists of a dextrorotatory terpene, boiling at 173° (343°·4 F.), and an oxygenated oil regarded by Gladstone as identical with carvol.

Oil of Anise, from the seed of *Pimpinella Anisum*, consists almost wholly of *anethol*, $C_{10}H_{12}O$, or $C_6H_4\left\{\begin{array}{l}OCH_3.\\C_3H_5\end{array}\right.$ The terpene, which is only present in small quantity, has not been examined.

Oil of Fennel, from the seeds of *Anethum Fæniculum*, also contains a large quantity of anethol, but is usually richer in terpene than anise oil. The terpene is dextrorotatory.

Oil of Cumin, distilled from the seeds of *Cuminum Cyminum*, consists chiefly of *cumic aldehyde*, $C_{10}H_{12}O$, and *cymene*, $C_{10}H_{14}$; but it also contains a terpene which when pure boils at about 165° (329° F.) (Beilstein and Kupfer, *Ann. Chem. Pharm.*, clxx. 284). According to Trapp (*ibid.* cviii. 386), the oil from the seeds of the Water Hemlock (*Cicuta virosa*) has the same composition as cumin oil.

Oil of Coriander, from the seeds of *Coriandrum sativum*, is said to consist of an oxygenated oil of the composition $C_{10}H_{18}O$.

Oil of Galbanum.—The oil which is separated from Galbanum resin by distillation with water consists of a dextrorotatory terpene, boiling at 160°—165° (320°—329° F.). It yields a crystalline hydrochloride.

Oil of Ajowan.—This oil, which is distilled from the fruits of *Ptychotis Ajowan*, an annual herb grown in Egypt and Persia, and especially in India, consists chiefly of *thymol*, $C_{10}H_{14}O$, and *cymene*, $C_{10}H_{14}$, but also appears to contain a terpene.

TERPENES FROM LABIATÆ.—*Oil of Thyme*, distilled from the *Thymus vulgaris*, the common garden thyme, has nearly the same composition as oil of ajowan, consisting chiefly of thymol and cymene, together with a lævorotatory terpene (*thymene*), boiling at 160°—165° (320°—329° F.).

Oil of Spearmint.—The oil extracted from the *Mentha viridis*, or ordinary garden mint, contains a dextrorotatory terpene, boiling at about 160° (320° F.), and an oxygenated oil, *menthol*, $C_{10}H_{14}O$, which, according to Gladstone, is isomeric with thymol, carvol, and myristicol.

Oil of Peppermint.—The essential oil of *Mentha piperita* appears to consist of a terpene and oxygenated compounds, but it has not been satisfactorily examined. When exposed to a low temperature, it sometimes deposits crystals of *Peppermint camphor*, $C_{10}H_{18}O$, also known as *menthol.* Chinese oil of peppermint, distilled in Canton from a plant which appears to be *Mentha arvensis* var. *Javanica*, contains a considerable amount of menthol and a liquid isomeride.

Oil of Lavender, from *Lavandula vera*, the common lavender, and *oil of Spike*, distilled in the south of France, from *Lavandula spica*, have not been properly examined; they contain hydrocarbons and oxygenated compounds. A solid substance is sometimes deposited from oil of lavender in cold weather, which is said to be identical with common camphor.

Oil of Rosemary, from *Rosmarinus officinalis*, consists almost wholly, according to Gladstone, of a feebly dextrorotatory terpene, boiling at about 163° (325°·4 F.); according to Lallemand, it is resolved by distillation into a lævorotatory terpene and an oxygenated portion, boiling at 200°—210° (392°—410° F.), which deposits at a low temperature a large quantity of camphor resembling common camphor in all respects, excepting that it has less dextrorotatory power.

Terpenes from the Oil of Eucalyptus Globulus.—According to Faust and Homeyer (*Deut. chem. Ges. Ber.*, vii. 1429), about nine-tenths of this oil consists of a mixture of a terpene boiling at 172°—175° (341°·6—347° F.), with cymene, in the proportion of about two parts of the former to one of the latter; the remaining portion consisting of an isomeric terpene, which boils at about 151° (303°·8 F.), and an oxygenated oil boiling at about 217° (422°·6 F.), which probably has the composition $C_{10}H_{18}O$.

Further particulars as to the essential oils may be obtained by consulting Hanbury and Flückiger's *Pharmacographia* (London, 1874); Gmelin's Chemistry (vol. xiv.); and the original papers of Gladstone (*Journ. Chem. Soc.* [2], II. 1.; xxv. 1), and Wright (*ibid.* xxvi. 549, 686; xxvii. 317, 620).

It will be evident, from what has just been stated, that our knowledge of the terpenes which are present in the various essential oils is extremely imperfect; in fact, it cannot be said that any one of the terpenes, with the exception of terebenthene, has been separated in a state of purity, and examined in such a way as to thoroughly establish its nature. This is mainly owing to the great difficulty of separating them from the substances with which they are associated in the essential oils.

But even with our present imperfect knowledge, it is evident that there is a close relationship between the terpenes furnished by plants of the same order, and it is not unlikely that many will be found identical. Thus the *Aurantiaceæ* furnish hydrocarbons with high boiling points (about 175°), which readily combine with hydrochloric acid, forming *di*hydrochlorides, and therefore resembling isoterebenthene (1270); the terpenes from the *Lauraceæ*, on the other hand, boil uniformly at much lower temperatures (about 160°), and appear rather to resemble terebenthene (1267).

It is therefore a matter of the utmost importance that the terpenes from a number of plants of the same order should be carefully comparatively studied, their physical properties determined, and their compounds with hydrochloric acid, &c., investigated in somewhat the same manner that terebenthene has recently been examined by Riban. It is difficult to over estimate the value of such an investigation of the terpenes, and of the essential oils yielding them, regarded as a contribution to the chemistry of plant life.

(1279) CAOUTCHOUC OR INDIAN RUBBER: $(C_8H_8)^x$.—This substance and Gutta Percha may be appropriately described here, since both are in a measure related to the terpenes. Caoutchouc occurs in small quantities in the juices of many plants, particularly of the *Urticaceæ*, *Euphorbiaceæ*, and *Apocynaceæ*. Its chief source, however, is the spontaneously solidified milky juice of the *Hævæa elastica*, *Jatropha elastica*, and some other tropical plants. As first procured by incisions into the stem of the plant, it appears as a yellowish milky fluid which, in addition to caoutchouc, contains albumin; the albumin causes the juice on being boiled to coagulate. When the fresh juice is exposed to the air in thin films, it speedily dries, and hardens into elastic layers of brownish-yellow caoutchouc. The caoutchouc is not dissolved in the juice, but is merely suspended in it, and when the liquid is diluted with water it rises to the surface like cream; when once it has become coherent it cannot again be diffused through water. In its solid condition it is extremely elastic, especially when warm. Its specific gravity varies from ·92 to ·96. Although insoluble in water, it softens considerably in this liquid at the boiling temperature, and is thereby rendered more easily acted upon by solvents. Caoutchouc may be preserved unaltered for an indefinite time if excluded from the light, but if exposed to the air for a few months in diffused daylight, it gradually absorbs oxygen and becomes converted into a viscid mass which has lost its elasticity, and is soluble in alcohol (W. A. Miller on Electric Cables, *Journ. Chem. Soc.*, 1865, 273). Alkaline solutions are without effect upon caoutchouc. Even chlorine attacks it very slowly; whilst concentrated sulphuric acid decomposes it slowly, concentrated nitric acid acts rapidly, when dilute, however, these acids are entirely inert. Commercial caoutchouc, from the mode of its preparation, necessarily retains the albumin and other constituents of the juice, but pure caoutchouc consists wholly of carbon and hydrogen in the proportions corresponding with the empirical formula, C_8H_8 (Faraday). This substance, however, is chiefly a mixture of *two* bodies, one much more soluble in ether, benzene, and similar liquids than the other (Payer).

Caoutchouc is insoluble in alcohol, but in contact with ether, chloroform, carbonic bisulphide, coal naphtha, or rectified oil of turpentine, it first swells up very considerably, and eventually forms a ropy liquid, which on evaporation leaves the caoutchouc with its original elasticity. This property is turned to account in the manufacture of various waterproof or "Macintosh" articles. The liquid thus formed is not a true solution, but a mixture caused by the interposition of the dissolved portion between the pores of the insoluble substance which is considerably swelled up, and has thus become easy to disintegrate. By employing a sufficient quantity of these solvents, renewed from time to time without agitation so as not to break the tumefied portion, the caoutchouc may be completely separated into two parts—viz., a substance perfectly soluble, ductile, and adhering strongly to the surface of bodies to which it is applied; and another substance, elastic, tenacious, and sparingly soluble. Caoutchouc is also dissolved by the fixed oils, but its elasticity is thereby destroyed. Waterproof cloth is prepared by varnishing one surface of a fabric constructed for the purpose, with a solution of caoutchouc, then bringing it into contact with a second sheet similarly prepared, and passing the two together between rollers. The freshly cut edges or surfaces of a piece of caoutchouc cohere readily; this property, with its pliancy and elasticity, together with its power of resisting most chemical agents, render it invaluable in the laboratory for forming the flexible tubes and joints used in connecting apparatus in a secure and air-tight manner. Caoutchouc melts at a heat of about 125° (257° F.); after it has been melted it does not solidify on cooling, but forms a sticky mass which does not become solid even when exposed to the air for months. Owing to this property it furnishes a valuable material for the lubrication of stopcocks and joints intended to remain moveable yet air-tight. If caoutchouc be heated strongly in the open air it takes fire, and burns with a bright luminous flame.

If distilled in closed vessels, caoutchouc furnishes a mixture of several hydrocarbons, amongst which are isoprene, C_5H_8 (1254); a *terpene* boiling at about 170° (338° F.), which Himly terms *caoutchin;* and a hydrocarbon boiling at about 315° (599° F.), *heveene*, which probably has the composition $C_{20}H_{32}$. The nature of the remaining products is not satisfactorily established, but from the composition of these several hydrocarbons it appears that the decomposition of caoutchouc by heat is merely the resolution of a complex hydrocarbon into simpler polymeric hydrocarbons.

(1280) A highly valuable modification of caoutchouc, discovered by Goodyear, is known in the arts under the name of *vulcanized* Indian rubber, which from its almost perfect elasticity at all temperatures below that of 115° (239° F.) admits of a variety of useful applications. The cut edges of this form of caoutchouc do not cohere by pressure, and it does not become adhesive to other bodies at a temperature below 100° (212° F.). Caoutchouc when immersed in the form of sheet in melted sulphur at 125° (257° F.), gradually imbibes from 12 to 15 per cent. of its weight of sulphur, but it does not at this temperature experience any change in its physical or chemical properties. If, however, such sulphurized rubber be heated for a few minutes to about 150° (302° F.), the peculiar elastic modification is produced, and if the temperature be allowed to rise much higher than this, the mass becomes black, hard, and horny, and is changed into *vulcanite* or *ebonite*, which may be applied to many of the purposes for which horn is fitted. At a temperature a few degrees beyond that necessary to the production of vulcanite the mass is converted into a hard brittle substance, which at a higher temperature undergoes carbonization and decomposition. Ebonite is largely prepared for the manufacture of combs, and articles such as were formerly made of papier-mâché, the proportions used being 2 parts of caoutchouc to 1 of sulphur. Exposure for some hours to a heat of from 150° to 180° (302° to 356° F.) effects the conversion. Ebonite, or vulcanite, is one of the best insulators of electricity that is known, and becomes powerfully negatively electric when excited by friction. The elastic vulcanized caoutchouc appears to consist of a combination of the original substance with 2 or 3 per cent. of its weight of sulphur. The excess of sulphur which is usually present is only mechanically distributed through the mass, and may be removed by the use of solvents, such as benzene or sodic sulphite. This excess of sulphur is injurious to the elasticity of the material, and gradually renders it brittle and rotten. Several modes of effecting the combination of sulphur with caoutchouc are employed. One of the most usual consists in grinding the caoutchouc between heated rollers with the proper proportion of sulphur: the mixture of caoutchouc and sulphur is left endued with the properties of common caoutchouc, and may be easily moulded into the form of the various articles required; it is only on the application of a temperature ranging from 130° to 150° (266° to 302° F.) that the peculiar properties of the sulphurized compound are developed. The heat is most advantageously applied by exposing the articles to the direct action of high-pressure steam at 132° to 137° (270° to 279° F.). A still easier method adapted for thin articles consists in immersing the caoutchouc for a few moments in a solution of 1 part of chloride of sulphur, S_2Cl_2, in 60 of carbonic bisulphide: by simple exposure of the object thus treated to the air, it assumes the character of vulcanized caoutchouc without the aid of heat. The addition of a certain proportion of carbonate of lead to the preparation is found to produce an article better adapted for some purposes, such as the manufacture of overshoes or goloshes, than one in which sulphur only is used; due proportions of sulphur and of the salt of lead are incorporated with the caoutchouc by causing the caoutchouc mixed with the other ingredients to pass repeatedly between polished hollow iron rollers maintained at a temperature of about 75° (167° F.), by the injection of steam into their interior. Vulcanized Indian rubber withstands prolonged digestion in naphtha or turpentine-oil without undergoing solution.

(1281) GUTTA PERCHA.—This substance, which is similar in chemical properties to caoutchouc, was introduced into this country as an article of commerce about the year 1844. Gutta percha is the concrete juice of the *Isonandra percha*, a tree belonging to the family of the *Sapotaceæ*, which grows abundantly in Singapore, Borneo, and other islands of the eastern archipelago. The name *percha* is that given by the Malays to the tree which produces it; it grows to a diameter of 5 or 6 feet, and although it is valueless as timber, the fruit yields an oil fit for food. On cutting notches through the bark into the wood, a milky juice exudes, which speedily solidifies. Gutta percha is a tough inelastic substance, which at ordinary temperatures retains any shape which may have been impressed upon it, but somewhat below 100° (212° F.) it becomes so soft that it may be moulded like wax, and indeed may be employed for taking casts and impressions, since it will copy the finest lines with fidelity; beautiful mouldings, and a variety of useful and ornamental articles are thus made with great facility. It also possesses the valuable property of welding together when in this soft condition, provided that the surfaces are quite free from any film of moisture. Below 45° (113° F.) it again becomes hard, and is possessed of extraordinary tenacity. It is, when pure, of a pale brown colour, possessing a peculiar odour somewhat resembling that of caoutchouc. When rubbed it becomes negatively electric, and if dry it is an insulator of electricity; this property has led to its extensive employment in the covering of wires for telegraphic purposes. It is also largely used as a waterproofing material, and is employed as a substitute for leather in soling boots and shoes. It furnishes a valuable material for the preparation of tubes for conveying liquids, and is likewise used as a substitute for leather in the construction of bands for driving machinery.

Gutta percha is quite insoluble in water; it is not attacked by linseed oil, but is dissolved readily by benzene, chloroform, carbonic bisulphide, oil of turpentine, and the essential oils in general with the aid of heat. If heated moderately it melts; and at a higher temperature is decomposed, yielding hydrocarbons identical with those from caoutchouc (Greville Williams). Solutions of the alkalies are without action upon gutta percha. Hydrochloric acid, and dilute hydrofluoric acid, as well as the dilute acids in general, have no action upon it; hence it is employed in the preparation of bottles and vessels used for containing these liquids. The principal drawback to this use is the difficulty of preventing it from retaining a certain degree of porosity, which allows the slow transudation of liquids through its mass. Concentrated nitric acid attacks and disintegrates it rapidly, whilst sulphuric acid produces the same effect more gradually.

Purified commercial gutta percha consists of three distinct substances; the most abundant of these, the *pure gutta*, which constitutes from 75 to 82 per cent. of the mass, is a hydrocarbon of the same percentage composition as the terpenes; it is insoluble in alcohol. The other two constituents are a white crystalline substance termed *alban*, $C_{20}H_{32}O_2$, insoluble in cold, but soluble in boiling alcohol; and an amorphous yellow resinous substance termed *fluavil*, $C_{20}H_{32}O$, soluble in cold alcohol. These two are probably produced by the oxidation of the pure gutta, which appears to take place during the extraction of the gutta percha from the trees. Pure gutta may be prepared by exhausting gutta percha with water and hydrochloric acid, and treating the residue with boiling ether (which dissolves everything except a few black flocks), leaving the filtrate to cool, pressing the substance which separates, and repeating the treatment until the ethereal liquid retains nothing in solution after cooling (Baumhauer). It is perfectly white when reduced to a fine powder; when heated it cakes together, and at 100° (212° F.) becomes transparent, whilst at 150° (302° F.) it begins to melt and is converted into a tenacious mass; at 180° (356° F.) an oily liquid begins to distil over; at 210° (410° F) the mass becomes filled with vapour-bubbles, and at 280° (536° F.) it froths strongly. Pure gutta percha slowly absorbs oxygen when exposed to the combined influence of light and air, and is gradually converted into a brittle resin freely soluble in hot alcohol. After having undergone this change it entirely loses its plastic character, and this is one of its principal defects; it may, however, be preserved in the dark or under water, for an indefinite period without change.

§ V. HYDROCARBONS OF THE C_nH_{2n-6}, OR BENZENE SERIES.

During the past few years more attention has been paid to the hydrocarbons of this series and their derivatives than to any other group of compounds, and their investigation has furnished results of great value, especially in connexion with the problem of isomerism. The first term of this series is *benzene*, C_6H_6, and a considerable number of other hydrocarbons exist which may be regarded as true homologues of it, since they exhibit the same general properties. Besides these, a hydrocarbon isomeric with benzene is known, possessing, however, altogether different properties, and also several hydrocarbons of the composition $C_{15}H_{24}$. The latter have been separated from certain essential oils, but it is not known at present whether they are true homologues of benzene, or whether they belong to an isomeric series.

As the chief source of benzene and several of its homologues is coal-tar, one of the products of the destructive distillation of coal, it will be convenient in this place to describe briefly the process of distilling coal and some other vegetable and animal substances before discussing benzene and its homologues.

Destructive Distillation of Vegetable Substances.

(1282) *Products of the Distillation of Coal.*—When a bituminous coal is burned in the open air, the principal products of the combustion are carbonic anhydride and water, with small quantities of ammonia and sulphurous anhydride, derived from the nitrogenized constituents and the pyrites contained in the coal; a certain portion of carbonaceous matter in a finely divided form escapes combustion, and constitutes the soot or visible smoke of a coal fire. When, however, the decomposition of the coal is effected in vessels from which the air is excluded, the products are much more numerous and complicated : a large amount of volatile matter is expelled, partly in the form of uncondensable gases, and partly in the form of vapours, which, when cooled to the ordinary temperature, become liquids or solids; whilst a large proportion of the combustible material remains behind in the retort, and forms a light, porous variety of coke, known as *gas coke.*

Amongst the gaseous products, the most important are methane, ethylene, hydrogen, carbonic oxide, carbonic anhydride, sulphuretted hydrogen, and ammonia. The liquid portions contain water, and various hydrocarbons, such as benzene, toluene, xylene, and pseudocumene, which constitute the chief ingredients of the liquid termed *coal naphtha* ; besides which there is a large quantity of a dark viscous matter, known as *coal-tar.*

When coal gas is to be employed for the purpose of illuminating the interior of a dwelling-house, it is not sufficient to condense the tar, the water, and other liquid products ; but it is also necessary to remove a number of gaseous compounds, before it can be burned with comfort, or even with safety to the health of the inmates. The impurities of which it is of most importance to deprive it are sulphuretted hydrogen and ammonia ; in addition to which carbonic anhydride and a small quantity of cyanogen are always removed during the purification. This purification is effected by submitting the gas to the action of certain chemical agents, particularly hydrated ferric oxide, and slaked lime.

The illuminating power of coal gas is due chiefly to olefiant gas or ethylene, butylene, and acetylene, but it is increased by the presence of a small quantity of the vapour of some other compounds of carbon and hydrogen. The hydrogen and carbonic oxide are not only destitute in themselves of any illuminating power, but they reduce the light of the gas with which they are mixed ; there is, however, no means of getting rid of these gases, so that care should be taken to produce as small an amount of them as possible during the process of carbonization.

(1283) *Manufacture and Purification of Coal Gas.*—The earliest attempts at illumination by means of coal gas were made by Mr. Murdoch, during his residence in Cornwall, about the year 1792, and he subsequently further carried out his plan, so as to illuminate a large portion of the manufactory of Boulton and Watt at Soho, at the celebration of the peace of Amiens in 1802. Ten years afterwards, the Chartered Gas Company, which made the first great experiment of lighting the streets by gas, was incorporated: and from that day to the present the employment of gas as a convenient and economical means of illumination has been steadily increasing. At the present time, upwards of one and a quarter million tons of coal are converted into gas annually in London alone; in addition to which every large manufacturing town, and many of the smaller towns and even villages in Great Britain, are lighted by gas; the use of gas is also general in the principal cities and large towns on the Continent.

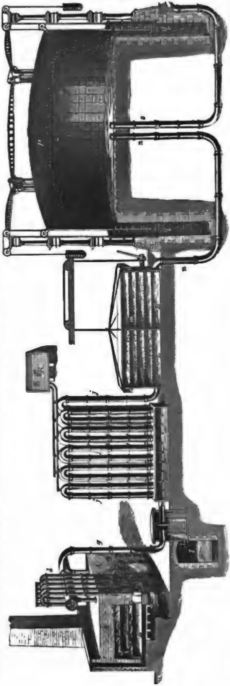
The proportion in which the different products of the distillation of coal are obtained, varies greatly, according to the kind of coal employed, and the temperature at which the distillation is conducted. The coal best suited to the manufacture of gas for illuminating purposes is of the variety known as bituminous. Anthracite is unfit for this use. The kind of coal employed in London for gas-making is principally that of the Durham coal field, or *Newcastle coal,* although it is not so well adapted to the purpose as some others, since it yields a gas of low illuminating power, which has usually to be brought up to the required standard by an admixture of cannel gas, obtained from cannel coal. A ton of good coal of this description yields on an average in London about 9250 cubic feet of gas of sp. gr. 0·410, and furnishes nearly a chaldron of coke weighing about 13 cwt. In coking, from 20 to 35 per cent. of fuel in proportion to the coal used (according to the judgment shown in constructing the furnace) is employed. The Scotch cannel coals furnish a gas of much higher illuminating power than that of the Newcastle coal, and of greater specific gravity, owing to the presence of a larger proportion of the denser hydrocarbons, although the volume of gas produced per ton is somewhat smaller, and the coke produced is of an inferior quality.

Fig. 391 gives a general view of the arrangement of the apparatus required in the manufacture and purification of coal gas; and the following is an outline of the process adopted:—

Pit-coal is heated in hollow flattened cylinders of iron, or more generally of clay, B B, set in stacks of from seven to ten, in long brick furnaces, A A. The mouths, *c c*, of these cylinders or retorts project from the brickwork, and are fitted with moveable lids, which can be closed air-tight by means of clay luting. From the upper side of the projecting extremity of each retort, a tube, *d*, for the conveyance of the gas, passes vertically upwards for a few feet, then forming an arch, dips downwards, terminating at *e*, beneath the level of the liquid contained in a long and wide pipe, *f*, called the *hydraulic main*, which passes horizontally along the front of the range of furnaces. This pipe is kept constantly half full of tar and condensed aqueous vapour. By this means the opening into each retort is effectually closed by a water valve, which permits a charge to be drawn and renewed in any one or more of the retorts, without interfering with the operation of those which are still in action. The tar, as it accumulates in the hydraulic main, flows over into the *tar wells*, H, I. In about four hours after charging the retort, the coal will have given off nearly all its gas, and a fresh charge of coal will be required; but it is not an unusual practice to charge the retorts only at intervals of six hours, since the gas, although poorer in quality, is increased in quantity, and the coke is improved by longer heating. When a charge is to be drawn, the mouth of the retort is opened, and the coke raked into large iron boxes, in which it is extinguished by pouring water over it. A fresh supply of coal is then introduced by means of a long scoop, so that the whole of the required quantity of coal is placed at once upon the floor of the retort, which is at a bright red heat. The door, which has been prepared with fresh luting upon its edges, is instantly replaced, and the distillation proceeded with. In large gas works the retorts are so arranged that a fresh set shall require charging every hour, in order that the gas which is produced shall at all times be nearly uniform in quality. The gas first given off is the best, and also the largest in quantity, the coal not having had time to rise to the full temperature of the retort. If the charge be exposed to heat for five hours, much of the gas in the last hour and a half consists of hydrogen and carbonic oxide, the coal having become thoroughly red hot throughout.

Having deposited in the hydraulic main most of the tar and some water, containing in solution a good deal of ammonic carbonate and hydric sulphide, the gases pass next through the pipe, *g*, to the *refrigerators* or *condensers*, *j j*, a series of serpentine or contorted tubes; these are kept cool by the extent of surface which they expose to the air, and their temperature, when necessary, may be reduced still

FIG. 391.



further, by allowing cold water from the cistern, K, to trickle over their exterior: here most of the remaining tar and aqueous vapour become separated. The gas now passes into an apparatus termed a *scrubber*, consisting of a tower, the interior of which is filled with small coke resting upon perforated shelves; through this mass of porous material a constant supply of fresh water is maintained, and by this arrangement the gas, which enters at the bottom of the tower, is exposed to a large absorbent surface, and the ammonia is effectually removed. This washing, however, somewhat diminishes the illuminating power of the gas, by removing a portion of the vapour of some of the more condensable hydrocarbons which are held in suspension.

From the scrubber the gas passes to the *purifiers*, L L′, which consist of cast-iron vessels containing a number of horizontal perforated shelves, *m m*, arranged one above another; upon each of the lower shelves a mixture of hydrated ferric oxide with moistened sawdust is placed to the depth of about five inches, whilst the upper shelf is usually filled with dry slaked lime. The gas enters at the bottom of the purifiers, and rises on one side through each layer in succession, descending on the other side of the purifier until it makes its exit at *n*. In these purifiers the gas loses carbonic acid, sulphuretted hydrogen, sulphocyanogen, cyanogen, and traces of naphthalene, which are still suspended in it.

Although the iron method above described is now almost universally adopted in large works, the most effectual way of removing the sulphuretted products from the gas is to cause it to bubble up through milk of lime; but the heavy pressure necessary to drive the gas through the liquid is such a disadvantage that it is preferable, where lime alone is used, to slake it and, after slightly moistening it with water, to place it on sieves or trays in a manner similar to the iron oxide. The spent lime, however, in both instances is of such an offensive nature that these methods cannot be conveniently used except where the works are quite isolated.

The gas, after it has been purified, is stored up for use in immense reservoirs or gasometers of metal, P, each consisting of a large bell of sheet iron, inverted in a brickwork tank, *q*, filled with water, in which the bell rises and falls. The bell is in some cases nearly counterpoised by weights attached to chains, which pass over pulleys suitably supported; but it is now more usual to construct them so as to rise and fall by the admission or escape of the gas without the necessity for any counterpoise. The pressure, which is not usually allowed to exceed that of a column of water two or three inches in height, drives the gas along the pipes or *main*, *o o*, by which it is distributed to the various consumers.

In the foregoing process one of the points of greatest importance is the due regulation of the temperature during the distillation. The retorts should be heated to a bright cherry-red. If they are insufficiently heated, the products will contain a large quantity of the vapours of condensable hydrocarbons, which collecting in the gasometers and the distributing pipes, would occasion much loss and inconvenience; whilst if the temperature is too high, or if the gas after its production is allowed to remain long in contact with the highly heated surface of the retort, it undergoes partial decomposition; a portion of its carbon is deposited, and forms a dense layer upon the interior of the retort, which it gradually chokes up, and at the same time the illuminating power of the gas is proportionately diminished by the loss of this carbon.

In addition to this inconvenience, carbonic bisulphide is formed in small quantity (the London gas contains from 7 to 10 grains in 100 cubic feet; Hofmann), especially if the distillation be conducted at too high a temperature. Dr. Angus Smith has proposed the use of a solution of oxide of lead in caustic soda, diffused through sawdust, for the purpose of absorbing the bisulphide, and the plan is said to succeed on the large scale; the use of the ammoniacal liquor in a scrubber to absorb this impurity has also been suggested. When gas which contains carbonic bisulphide is burned, a minute quantity of sulphuric acid is formed, which gradually accumulates on the furniture of the building, on the binding of books, &c., and slowly corrodes and otherwise injures them.

(1284) *Compounds present in Coal-tar.*—Coal-tar varies in density from 1·120 to 1·150; the lightest tar containing the largest proportion of liquid oils. Of the substances contained in coal-tar some are basic and some acid, but the principal portion consists of neutral or indifferent bodies.

The following is a list of the compounds the existence of which in coal-tar has been satisfactorily established:

	Name.	Formula.
	Carbonic bisulphide ...	CS_2
	Acetic acid	$C_2H_4O_2$
C_nH_{2n+2} series.	Hexane	C_6H_{14}
	Heptane	C_7H_{16}
	Octane	C_8H_{18}
	Decane	$C_{10}H_{22}$
	Solid paraffins ...	C_nH_{2n+2}
C_nH_{2n} series.	Amylene	C_5H_{10}
	Hexylene	C_6H_{12}
C_nH_{2n-2} series.	Crotonylene	C_4H_6
	Hexoylene	C_6H_{10}
C_nH_{2n-6} series.	Benzene	C_6H_6
	Toluene	C_7H_8
	Paraxylene	C_8H_{10}
	Metaxylene	C_8H_{10}
	Pseudocumene ...	C_9H_{12}
	Mesitylene	C_9H_{12}
	Naphthalene... ...	$C_{10}H_8$
	Diphenyl	$C_{12}H_{10}$
	Acenaphthene ...	$C_{12}H_{10}$
	Fluorene	$C_{13}H_{10}$
	Anthracene	$C_{14}H_{10}$
	Phenanthrene ...	$C_{14}H_{10}$
	Pyrene	$C_{16}H_{10}$
	Chrysene	$C_{18}H_{12}$

	Name.	Formula.
$C_nH_{2n-7}OH$ series.	Phenol	C_6H_6O
	Paracresol	C_7H_8O
	Metacresol	C_7H_8O
	Orthocresol	C_7H_8O
	Pyrrol	C_4H_5N
	Aniline	C_6H_7N
$C_nH_{2n-5}N$ series.	Pyridine	C_5H_5N
	Picoline	C_6H_7N
	Lutidine	C_7H_9N
	Collidine	$C_8H_{11}N$
	Parvoline	$C_9H_{13}N$
	Coridine	$C_{10}H_{15}N$
	Rubidine	$C_{11}H_{17}N$
	Viridine	$C_{12}H_{19}N$
$C_nH_{2n-11}N$ series.	Leucoline	C_9H_7N
	Lepidine	$C_{10}H_9N$
	Cryptidine	$C_{11}H_{11}N$

The distillation of coal-tar is conducted on an extensive scale, as a separate branch of trade. The operation is performed in large cylindrical iron retorts of the capacity of from 1000 to 2000 gallons. The first portions that are volatilized consist chiefly of ammonia, accompanied by some permanent gases which have been dissolved by the liquid hydrocarbons. As the temperature rises, water charged with various ammoniacal salts comes over, and a fœtid brown oil gradually collects upon the surface of the water in the receiver. As the distillation proceeds, water ceases to come over, and the quantity of this oil increases, its density continuing to augment until its specific gravity exceeds that of water. The light oil amounts generally to from 5 to 10 per cent. of the tar. This distillate may be freed from compounds which rapidly absorb oxygen and cause the distilled oil to become brown on keeping, by agitation with a small portion of sulphuric acid, by which these oxidizable products are converted into a tenacious tarry mass denser than the rest of the oil, in which it is no longer soluble. The purified supernatant oil, when again rectified, constitutes *coal naphtha.* By continuing the distillation of the coal-tar, a yellow, heavy fœtid oil, technically known as *dead oil,* is obtained, the amount of which seldom exceeds 30 per cent. of the quantity of tar employed. In the latter stages of the operation, naphthalene is abundant in the distillate, and the oil becomes semi-solid as it cools. The black residue in the retort solidifies on cooling, and forms *pitch,* which is employed in the preparation of asphalte, and as a colouring ingredient in the production of a coarse black varnish, used for protecting iron-work from rust. If it be desired to carry the distillation further, a much higher temperature is required, when the pitch in its turn undergoes decomposition, and yields a product which, when cool, has the consistence of butter; it consists chiefly of *anthracene,* and some other hydrocarbons such as phenanthrene, acenaphthene, and fluorene. At a still more advanced stage of the process the distillate acquires a yellow colour, and assumes the appearance of a resin; whilst as the temperature of the retort approaches a red heat, the vapours produced become condensed in the form of a bright orange-coloured powder which is free from odour, and when pressed, agglutinates into a viscous mass. This substance consists chiefly of *pyrene,* $C_{16}H_{10}$, and *chrysene,* $C_{18}H_{12}$. The residue in the retort, after it has ceased to give off volatile matters, forms a hard porous coke, which is difficult of combustion.

The heavy coal-oil, or dead oil, is seldom submitted to further purification. It contains phenol, cresols, aniline and other basic substances, besides naphthalene and other hydrocarbons which boil between 200° and 300° (392° and 572° F.), and which hold a considerable quantity of anthracene in solution. Heavy coal naphtha, or dead oil, is remarkable for its antiseptic qualities, and is employed for the preservation of timber for railway sleepers, &c. It is also consumed as a fuel in lamps, and in specially constructed furnaces for heating purposes.

The light naphtha obtained in the foregoing process, after being agitated with a solution of caustic soda to extract the phenol and cresols, is submitted to rectification, by which it is separated into a more volatile portion, and an additional quantity of the heavy oil containing much naphthalene. It is usual to agitate the rectified portion with sulphuric acid, which thus acquires a deep red colour, and removes a large portion of the products which communicate to the crude distillate its offensive odour. The mixture, on standing, separates into two layers, the lighter of which is the purified naphtha. When this liquid is again submitted to distillation, the oil which comes over is almost free from naphthalene, and does not become coloured by exposure to the air. Coal naphtha thus purified and sold as 'highly rectified,' varies in specific gravity from about 0·860 to 0·900. It consists of a mixture of bodies which boil below 200° (392° F.), and may be separated from each other by distillation.

Mansfield was the first (*Journ. Chem. Soc.*, i. 252) to make a careful examination of the constituents of this naphtha. In his experiments he employed the crude light naphtha, before it had been treated with sulphuric acid; and having freed it from basic and acid bodies by agitating it successively with dilute sulphuric acid and a weak solution of potassic hydrate, he submitted it to a systematic process of fractional distillation. He thus found that at least five distinct liquids might be separated from light coal naphtha:—1. A mobile fluid of alliaceous odour, boiling below 70° (158° F.), which he did not examine, but which from the recent investigations of Helbing (*Ann. Chem. Pharm.*, clxxii. 281) appears to be a mixture of benzene with carbonic bisulphide, amylene, hexylene and crotonylene, C_4H_6. 2. A fraction boiling at about 80° (176° F.), consisting chiefly of benzene, C_6H_6, but as Schorlemmer has since shown (*ibid.* cxxxix. 244) also containing small quantities of hexoylene (1255), a hydrocarbon of the acetylene series. 3. A portion which distils at about 113° (235°·4 F.), consisting of toluene, C_7H_8. 4. A liquid boiling at 142°—145° (287°·6—293° F.) which he regarded as cumene, C_9H_{12}, but which Fittig's researches have proved to be chiefly para- and metaxylene; and 5. A liquid boiling at 170°—173° (338°—343°·4 F.): this Mansfield believed to be cymene, $C_{10}H_{14}$, but from Fittig's experiments it would appear to be impure cumene, C_9H_{12}. It is a mixture of at least two isomeric bodies—viz., mesitylene and pseudocumene.

Coal-oil does not seem to contain any appreciable quantity of hydrocarbons boiling between 170° and 200° (338° and 392° F.) (Fittig, *Deut. chem. Ges. Ber.*, viii. 22), whilst of the higher fractions, that which distils at 210°—220° (410°—428° F.) consists almost entirely of naphthalene, and that which comes over between 220° and 270° (428° and 518° F.) contains diphenyl and a mixture of liquid hydrocarbons which has not as yet been examined. The portions of still higher boiling point contain acenaphthene, fluorene, anthracene, phenanthrene, pyrene, and chrysene.

(1285) *Products of the Distillation of Cannel Coal and Lignite.*—The oily product obtained on distilling boghead or cannel coals and the bituminous shales at a comparatively low temperature, consists in great part of hydrocarbons of the paraffin series (p. 130), but it also contains various members of the olefine and acetylene series.

Lignite, when distilled, also furnishes paraffins, but at the same time an acid oil is produced which contains phenol and probably homologous substances also.

(1286) *Products of the Distillation of Wood.*—The substances which are formed during the destructive distillation of wood in closed vessels are very numerous. They vary with the nature of the wood operated on, and the temperature at which the distillation is effected. The decomposition commences slowly at a temperature of about 140° (284° F.). The volatile portion of the products includes substances which are gaseous, as well as those which are liquid or solid, whilst a considerable residue of charcoal is left in the retort. Amongst the gaseous products of the distillation, the most abundant are carbonic anhydride, carbonic oxide, and hydrogen. Of the liquid products one portion is soluble in water and another oily and insoluble. The soluble portion consists of acetic acid, methylic alcohol or wood spirit, ethylic alcohol, allylic alcohol, methylic acetate and acetone, accompanied by water, and by other bodies but imperfectly known. The insoluble portion, which constitutes *wood tar*, is composed of a mixture of various liquids holding solid matters in solution: its most important constituents are several hydrocarbons, amongst which are paraffins, benzene, toluene, xylene, and others which have been less perfectly examined, besides a number of oxidized compounds, including 'creasote.' Amongst the solid portions are 'paraffin,' and resinous matters more or less resembling colophony; there are also various other bodies, such as naphthalene, pyrene, chrysene, &c.

The products obtained at the lowest temperature, in the distillation of wood, are those into the composition of which oxygen enters abundantly, such as water, acetic and carbonic acids: as the temperature rises, compounds containing less oxygen are gradually formed, such as methylic alcohol or wood spirit, acetone, and creasote; at a still more elevated temperature various hydrocarbons, such as toluene, xylene, and the different paraffins are produced, whilst as the temperature approaches to redness, pure hydrogen predominates.

In the distillation in iron cylinders of air-dried hard woods, such as oak or beech, the charcoal amounts to about 25 per cent. of the weight of the wood employed, or about three-fifths of the quantity of carbon present in the wood. The liquid portion, amounting to about 53 per cent., contains nearly one-fifth of the entire quantity of carbon in the wood: and the remaining portion of the distillate, consisting of uncondensed gases, carries off the remainder of the carbon. Among the liquid products, acetic acid amounts to between 3 and 4 per cent. of the weight of the harder woods, naphtha to about 1 per cent., and the tar to 7·5 per cent.

(1287) *Stockholm tar*, so largely used in shipbuilding, is obtained by a rude kind of distillation of the resinous wood of the pine. A conical cavity is formed in the side of a hillock, the apex of the cone being below, and terminating in an aperture that opens into a trough leading to a reservoir for the tar. The kiln is filled with wood, and covered over incompletely with turf; the pile is lighted at the top, and the combustion regulated by covering it in more or less completely; the wood is thus charred from above downwards, and the tar flows off at the bottom, charged with a considerable quantity of resin, and mixed with acetic acid and oil of turpentine. When heated, an impure turpentine-oil is distilled, leaving a black resinous substance, which constitutes ordinary *pitch*. The specific gravity of the ordinary wood tar of commerce is about 1·040.

(1288) *Creasote* (from *κρέας*, flesh, *σώτὴρ*, preserver). Much of the creasote of commerce is simply phenol, but the true creasote of Reichenbach (*Pogg. Ann.*, xxi. 57; xxviii. 125; xxix. 162) is a distinct substance; to which indeed wood-smoke owes its characteristic odour and antiseptic qualities.

Preparation.—The process of purifying creasote is tedious. The heavier portions of the oil obtained from wood tar, after being washed with a solution of sodic carbonate, are submitted to distillation, by which they are further separated into a portion lighter than water, and into another which sinks in this liquid. This heavier oil is then treated with a solution of potassic hydrate of sp. gr. 1·12, which dissolves the creasote; the greater part of the hydrocarbons which accompanied it being separated. The alkaline solution, after being decanted from the layer of oily hydrocarbons, is boiled gently in an open basin, with a view to oxidize a portion of the impurities. When cold, dilute sulphuric acid is added to the liquid in slight excess, by which means the creasote is set free. It is, however, far from being pure, and must be redistilled with water, again treated with concentrated solution of potassic hydrate, then with dilute sulphuric acid, and finally redistilled with water. This series of operations is to be repeated as long as hydrocarbons continue to be separated. Lastly, the creasote should be digested with calcic chloride, and distilled by itself. Rhenish creasote begins to boil at 130° (266° F.), but the bulk of it distils at 199°—208° (390°·2—406°·4 F.), a smaller portion at 208°—216° (406°·4—420°·8 F.), leaving a dark-coloured residue.

Properties.—Creasote, when pure, is a colourless oily liquid, of high refractive power. It is not easily inflamed, but when kindled it burns with a smoky flame. Its taste is burning, and its odour extremely pungent and peculiar; if swallowed in doses of more than a few drops, it acts as a poison. Creasote is sparingly soluble in water, to which it communicates its peculiar odour and pungent taste. It is freely soluble in acetic acid, alcohol, and ether, as well as in benzene and carbonic bisulphide; solutions of the fixed alkalies and of ammonia also dissolve it. Creasote immediately coagulates albumin, and is one of the most powerful antiseptics known. Meat that has been plunged into a solution containing 1 per cent. of creasote gradually becomes dry and hard on exposure to the air, and acquires the flavour of smoked meat, but does not become putrid. A considerable portion of creasote (from 1 to 1½ per cent.) is held in solution in the crude pyroligneous acid obtained during the destructive distillation of wood, and on saturating this acid at 75° (167° F.) with effloresced sodic sulphate, an oily matter which contains a large proportion of creasote is separated. Crude pyroligneous acid, on account of the creasote which it contains, is frequently employed for preserving hams and salted provisions, to which it communicates the same flavour as if they had been exposed to wood-smoke.

Creasote when largely diluted is sometimes given internally in order to check obstinate vomiting. If applied in a concentrated form to the exposed pulp of a carious tooth, it frequently affords instant relief in cases of acute toothache. In a very dilute form, it is also a valuable application in some cases of fœtid ulcers, and in many cutaneous affections. If applied to the skin in a concentrated state it produces a white spot, the skin becoming disorganized, and peeling off without any attendant inflammation.

The researches of Hugo Müller, Gorup-Besanez, Marasse, and Tieman have shown that creasote is a complex mixture containing phenol, $C_6H_5.OH$; paracresol, $C_7H_7.OH$; phlorol, $C_8H_9.OH$; guaiacol, $C_6H_4.\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$; creosol, $C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$; methylguaiacol, $C_6H_4\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$; methylcreosol, $C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$, &c. (see *Alcohols*). The relative proportions of these compounds vary, however, in creasotes from different sources. There are other oxygenated compounds present in wood tar, but as yet they have been but very imperfectly examined (see *Cærulignone*).

(1289) *Distillation of Peat.*—The products furnished by the destructive distillation of peat, which is formed by the decomposition of vegetable matters, is probably of a nature somewhat similar to those obtained from wood, but they have never been carefully examined. The distillation was for some time carried on at Atley, near Kildare, in furnaces resembling an ordinary blast furnace. The crude products consist of tar, above which is a watery liquid, besides gaseous matters. The tar when purified by distillation in a current of superheated steam yields first a liquid, then one which is pasty when cold, and lastly a solid distillate, whilst about 5 per cent. of a porous carbonaceous mass is left in the retort. The liquid portion, after treatment with sulphuric acid, and redistillation, gives an oil fit for lubricating purposes, whilst solid paraffin may be extracted from the pasty portion. The aqueous liquid contains methylic alcohol, acetic acid, and ammonia.

(1290) *Products of the distillation of Menhaden Oil Soap.*—When the lime soap produced by saponifying menhaden oil (from the *Aloea menhaden*, a sort of herring) with milk of lime is distilled with excess of calcic hydrate, a liquid product is obtained, which has been examined by Warren and Storer (*Mem. Amer. Acad.*, N.S. ix. 177). They have succeeded in isolating the following hydrocarbons from it:

	Approximate B. P. (Cent.)
Paraffins: C_nH_{2n+2}	
C_5H_{12}	39°
C_6H_{14}	69°
C_7H_{16}	98°
C_8H_{18}	128°
Olefines: C_nH_{2n}	
C_5H_{10}	35°
C_6H_{12}	65°
C_7H_{14}	95°
C_8H_{16}	125°

	Approximate B. P. (Cent.)
Olefines : C_nH_{2n}	
C_9H_{18}	153°
$C_{10}H_{20}$	175°
$C_{11}H_{22}$	195°
$C_{12}H_{24}$	212°
Hydrocarbons of the C_nH_{2n-6} *series*	
C_6H_6	80°
C_7H_8	111°
C_8H_{10}	—
C_9H_{12}	—

(1291) *Products of the distillation of Bones.*—In the preparation of animal charcoal by igniting bones in iron cylinders, an oil is obtained which after rectification is known as *Dippel's animal oil.* This has been investigated by Anderson, who succeeded in isolating numerous substances from it. Although small quantities of paraffins, benzene, and probably homologous hydrocarbons are present, it consists chiefly of a mixture of nitrogenous substances of a basic character. Of these, various members belonging respectively to the series $(C_nH_{2n+1})H_2N$ and $C_nH_{2n-5}N$ have been isolated, viz.:

Methylamine	$CH_3.H_2N$	Pyridine	C_5H_5N
Ethylamine	$C_2H_5.H_2N$	Picoline	C_6H_7N
Propylamine	$C_3H_7.H_2N$	Lutidine	C_7H_9N
Butylamine	$C_4H_9.H_2N$	Collidine	$C_8H_{11}N$
Amylamine	$C_5H_{11}.H_2N$		

The oil also contains aniline, C_6H_9N, pyrrol, C_4H_5N, and other nitrogenous substances which are decomposed when heated with sodium.

(1292) BENZENE. *Benzol,* or *Phenylic hydride,* $C_6H_6=78$.—Benzene was originally obtained by Faraday in 1825 from the liquid produced by the compression of oil-gas, and was named *bicarburet of hydrogen ;* subsequently Mitscherlich found that the liquid obtained by distilling benzoic acid with an excess of lime contained the same body, and he named it *benzine.**

Benzene is produced in a very large number of reactions: thus it is formed amongst other products when acetylene is heated to about the temperature at which glass softens (Berthelot): $3C_2H_2=C_6H_6$. The higher homologues of benzene, and a number of hydrocarbons, such as naphthalene and anthracene, also yield benzene, together with other products, when heated to redness either alone or mixed with hydrogen (Berthelot). When phenol, $C_6H_5.OH$, is passed over strongly heated zinc dust, benzene is obtained (Baeyer): $C_6H_6O+Zn=C_6H_6+ZnO$. Pure benzene may be prepared by carefully distilling benzoic acid with calcic hydrate at a dull red heat: $C_7H_6O_2+Ca(OH)_2=C_6H_6+CaCO_3+OH_2$;

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* The substances which are now largely sold under the names of *benzine* and *benzoline* are chiefly mixtures of paraffins and do not contain benzene.

and similarly all the *benzene-carboxylic acids*, represented by the formula $C_6H_{6-n}(COOH)_n$, furnish benzene when distilled with calcic hydrate.

On the large scale, however, benzene is always prepared from the portion of coal-tar oil boiling below 100° (212° F.) in the following manner:

The oil is first agitated with dilute sulphuric acid, then with water, and finally with milk of lime, or a solution of sodic hydrate, in order to remove all the substances of basic and acid properties it may contain. In order to separate hydrocarbons of the C_nH_{2n} and C_nH_{2n-2} series which are always present, it is next digested on the water-bath with about $\frac{1}{10}$ of its weight of concentrated sulphuric acid for 8 to 10 hours in a flask attached to an inverted condenser; separated from the blackened acid mass, washed with a small quantity of water, and similarly treated a second or even a third time: until, in fact, the liquid is no longer coloured by the action of the acid. It is then submitted to fractional distillation, collecting apart the portion boiling below 90° (194° F.), in order to separate the homologous hydrocarbons; this distillate is cooled to a low temperature by a mixture of ice and salt: the benzene then crystallizes out, whilst the other hydrocarbons remain liquid, and may for the greater part be removed by draining the crystals on a vacuum-filter. If the benzene is required pure, these should be melted and recrystallized two or three times, carefully draining off the mother liquor.

Properties of Benzene.—It is a colourless, very limpid, strongly refracting liquid, of a peculiar and rather agreeable odour. Its specific gravity at 0° (32° F.) is 0·8995. It solidifies, on cooling, to a brilliant white mass of fern-like tufts, which melt at 5°·5 (41°·9 F.). Benzene boils at 80°·5 (176°·9 F.), and emits an extremely inflammable vapour, which burns with a highly luminous but very smoky flame. It is not appreciably soluble in water, but is freely soluble in alcohol, ether, acetone, oil of turpentine, and many other media. It dissolves entirely if heated at 100° (212° F.) for a few hours with 4 or 5 times its bulk of sulphuric acid, forming a colourless liquid if the benzene is quite pure. When hot it dissolves sulphur, phosphorus, and iodine; it is also an excellent solvent for caoutchouc and gutta-percha, and on evaporation it leaves them with their peculiar physical characters unaltered. It also dissolves wax and fatty bodies with facility; whilst its solvent power for fats and oils enables it to be used with advantage for removing grease stains from articles of silk or wool. As most colloid substances are insoluble in benzene, it is of great use in the chemical laboratory for purifying crystalline substances from the small quantities of colouring matters, &c., which often obstinately adhere to them.

When the vapour of benzene is passed through a tube heated to bright redness, *diphenyl*, $C_{12}H_{10}$, is produced (Berthelot), together with hydrogen, *paradiphenylbenzene*, $C_6H_4(C_6H_5)_2$, an isomeric body which is probably *orthodiphenylbenzene*, and small quantities of other hydrocarbons of unknown composition (Schultz, *Ann. Chem. Pharm.*, clxxiv. 228). According to Berthelot, a mixture of benzene vapour and ethylene passed through a red-hot tube yields *cinnamene*, C_8H_8, *naphthalene*, $C_{10}H_8$, *acenaphthene*, $C_{12}H_{10}$, *anthracene*, $C_{14}H_{10}$, and hydrogen.

Berthelot also states that benzene is not attacked by sodium; when it is heated to about 250° (482° F.) with potassium, however, a black mass is obtained, which is highly explosive, and is violently decomposed by water (Abeljanz, *Deut. chem. Ges. Ber.*, v. 1027).

When oxidized by the ordinary reagents, benzene does not furnish compounds containing the same number of carbon atoms, but is more or less completely converted into carbonic anhydride and water. By the action of chromic chloride, CrO_2Cl_2, on a solution of benzene in glacial acetic acid, however, *trichloroquinone* is produced (Carstanjen):

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Chromic chloride.}}{4CrO_2Cl_2} = \underset{\text{Trichloroquinone.}}{C_6HCl_3O_2} + 2Cr_2O_3 + 5HCl.$$

When oxidized by manganic peroxide and sulphuric acid, benzene furnishes, together with formic acid, carbonic anhydride and water, small quantities of *benzoic acid*, $C_6H_5.COOH$, *phthalic acid*, $C_6H_4(COOH)_2$ (Carius, *Zeits. Chem.* [2], iv. 505), and the isomeric *terephthalic acid* (Oudemanns, *ibid.* v. 84). The formation of these acids has been shown to be the result of the simultaneous oxidation of benzene and the formic acid generated by the oxidation of a portion of the benzene, thus:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Formic acid.}}{HCOOH} + O = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + OH_2.$$

$$\underset{\text{Benzoic acid.}}{C_6H_5.COOH} + \underset{\text{Formic acid.}}{HCOOH} + O = \underset{\text{Phthalic acid.}}{C_6H_4(COOH)_2} + OH_2.$$

According to Berthelot, benzene is almost wholly converted into hexane, C_6H_{14}, when heated for twenty-four hours to 280° (536° F.) with 80 parts of a saturated solution of hydriodic acid. Baeyer states that when benzene is heated with dry hydriodic acid gas even to 350° (662° F.), it is not affected. In the dark, or in diffused light, chlorine in presence of iodine and bromine both act slowly on benzene, at the ordinary temperature, and more rapidly on heating, producing mono-, di-, and even trichloro- and bromo-benzenes. The action of bromine at a high temperature gives rise to tetra- and penta-bromobenzenes (see

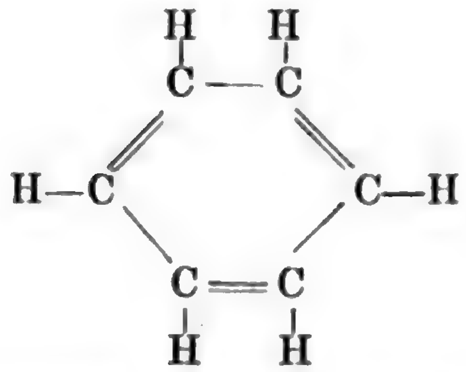
Haloid derivatives of benzene). Iodine alone has no action on benzene, but when a mixture of benzene with iodine and iodic acid is heated, iodobenzenes are formed. If, however, a mixture of benzene and chlorine or bromine is exposed to bright sunshine instead of diffused daylight, compounds of these elements with benzene are obtained: the bodies $C_6H_6Cl_6$ (*benzene hexachloride*, or *hexachlorohexylene*) and $C_6H_6Br_6$ are readily separated, but the intermediate compounds $C_6H_6Cl_2$, $C_6H_6Cl_4$, $C_6H_6Br_2$ and $C_6H_6Br_4$, which without doubt are simultaneously produced, cannot be isolated on account of their instability. Although benzene is not in the least acted on by the haloid acids, it unites with hypochlorous acid, forming the compound $C_6H_6Cl_3(OH)_3$, the so-called *trichlorhydrin of phenose*. By the action of chlorous acid on benzene the so-called *trichlorophenomalic acid* is produced, together with chlorobenzene and dichloroquinone (Carius, *Ann. Chem. Pharm.*, cxlii. 129):

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Chlorous acid.}}{3HClO_2} = \underset{\text{Trichlorophenomalic acid.}}{C_6H_7Cl_3O_5} + OH_2.$$

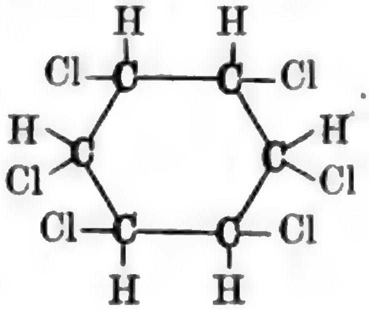
By the action of concentrated nitric acid, benzene is readily converted into *nitrobenzene*, $C_6H_5.NO_2$; which, by the further action of the acid, becomes *dinitrobenzene*, $C_6H_4(NO_2)_2$. Benzene, when warmed with concentrated sulphuric acid, furnishes *benzenesulphonic acid*, $C_6H_5.SO_3H$; and the same acid is formed together with *benzenesulphonic chloride*, $C_6H_5.SO_2Cl$, and *benzenesulphone* or *sulphobenzid*, $(C_6H_5)_2SO_2$, by the action of chlorhydric sulphate, $SO_2Cl.OH$, on benzene. Sulphuric anhydride converts benzene into benzenesulphonic acid and benzenesulphone. When heated with sulphuric chloride, SO_2Cl_2, to 150° (302° F.), benzene is converted into *mono*chlorobenzene:

$$SO_2Cl_2 + C_6H_6 = SO_2 + C_6H_5Cl + HCl.$$

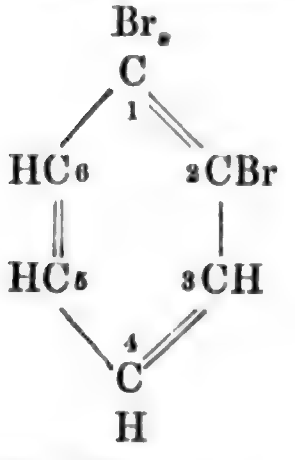
Constitution of Benzene.—Benzene behaves in the majority of cases as a saturated compound, inasmuch as it tends always to form *substitution* derivatives; and when *additive* compounds are formed it unites with at most *six* atoms of a monad. Kekulé in 1865 was the first to propose a consistent theory to account for this peculiar behaviour of benzene. He supposed that the six atoms of carbon are united alternately by one and two affinities of each, so as to form a *closed chain*, and that the remaining affinity of each carbon atom is saturated with hydrogen; this may be indicated by the following diagram:



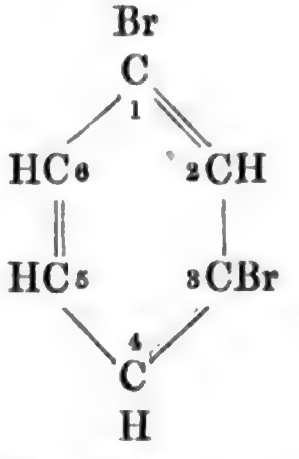
In the additive compounds, formed by the addition of six monad atoms to benzene, the carbon atoms are united by single affinities, but the closed chain is preserved; thus:



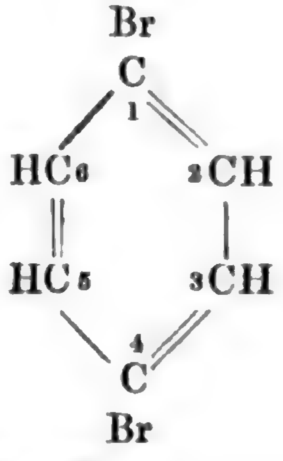
The hypothesis that the six atoms of hydrogen are of equal value was also adopted as the simplest and most probable, and this has since been abundantly justified by the fact that no isomeric mono-substitution derivatives have been obtained from benzene. Several isomeric modifications of the higher substitution derivatives were known to exist however, and Kekulé explained this in a very simple manner by supposing the phenomena to be due to a difference in the relative positions of the substituting radicles. Thus, if for convenience of reference the six atoms of carbon are indicated respectively by the figures 1, 2, 3, 4, 5 and 6, and we suppose that in monobromobenzene, for example, the bromine occupies the position 1, then according as a second atom of the bromine is introduced in the position 2, 3, or 4, we obtain three dibromobenzenes, in which the bromine atoms occupy relatively different positions:



Br : Br = 1 : 2

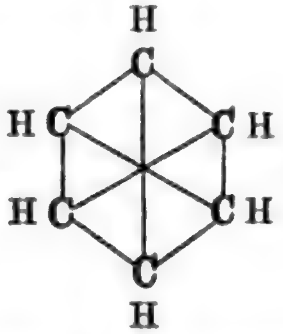


Br : Br = 1 : 3

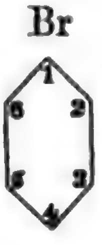


Br : Br = 1 : 4

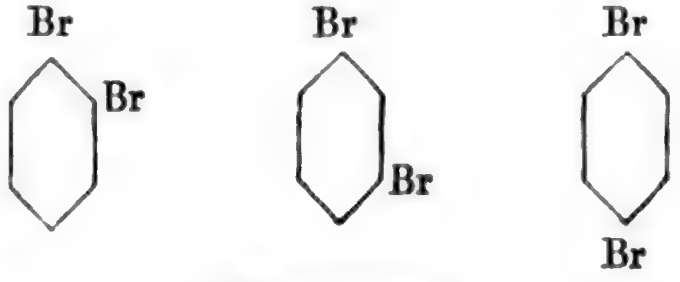
Kekulé supposed that the positions 5 and 6 were relatively identical with 2 and 3, and therefore that only *three* isomeric di-derivatives of benzene were possible.* It has, however, been urged that in this scheme the positions 2 and 6 cannot be identical, because in the one case the two carbon atoms (1 and 2) are united by double affinities and in the other (1 and 6) by single affinities, and that accordingly *four* isomeric di-derivatives should exist; but inasmuch as only three have ever been obtained, it has therefore been proposed to slightly modify Kekulé's hypothesis, and to suppose that each atom of carbon is in direct union with three other carbon atoms, somewhat in the manner indicated by the diagram:



All other facts with regard to benzene are capable of expression by this formula, and the impression is gaining ground that it merits the preference over that originally proposed by Kekulé as a graphic representation of the known reactions of benzene. (See *Summary of the Action of Reagents on Benzene.*) Whatever hypothesis we accept as to the mode of union of the carbon atoms in benzene, however, Kekulé's original explanation of the cause of isomerism among the benzene derivatives still holds good. Moreover, the constitution of the isomeric benzene derivatives may be conveniently expressed graphically, without reference to the constitution of benzene itself, by the employment of a simple hexagon to represent benzene, the substituting radicles merely being written at the corners in their appropriate positions, thus:



Monobromobenzene.



Dibromobenzenes.

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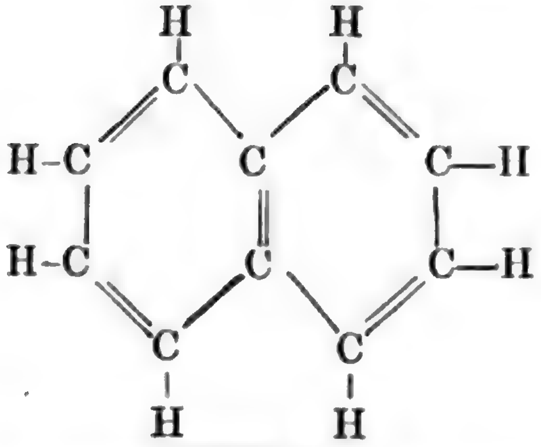
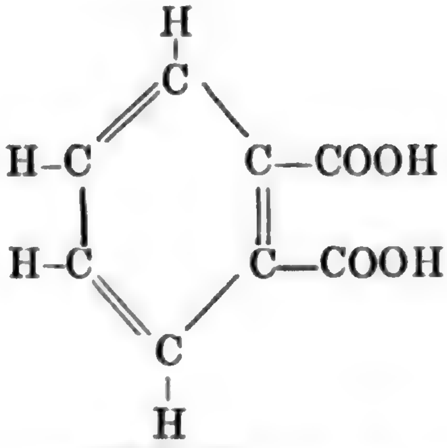
* Kekulé has discussed at length the reasons which lead him to regard the positions 2 and 6 as identical; and an account of his views will be found in Watts' "Dictionary of Chemistry," Second Supplement, p. 132.

Determination of the Constitution of Benzene Derivatives.—Kekulé's explanation of isomerism has not only been almost universally accepted, but much attention has been devoted by chemists for several years past to the determination of the relative positions which the radicles occupy in the various substitution derivatives of benzene.

Obviously, it would appear to be a simple matter to arrange all the derivatives in which substitution has taken place to the same degree in groups, in such a manner that each group shall only contain substances which are convertible either into one another, or into a third body in which substitution has also taken place to the same degree, provided that in the formation of the one from the other, isomeric change, or change of position of the radicles, has not taken place. These substances may all be regarded as members of one group; and if the constitution of any one member of such a group can be determined, it is clear that we are then in a position to infer that of the other members. Notwithstanding the apparent simplicity of the problem, chemists long differed greatly as to the arrangement of the various benzene derivatives in groups of similarly constituted bodies, and have only recently arrived at a satisfactory result. The problem of the determination of the constitution of the members of the various groups, which it need scarcely be said is far more difficult, has also given rise to much discussion.

According to Kekulé's hypothesis, as above stated, although isomeric mono-derivatives of benzene cannot exist, the di-derivatives are capable of existing in three isomeric modifications; and the experimental results hitherto obtained are in complete accordance with theory in this respect. It has been very generally the custom to refer the di-derivatives of benzene to the three isomeric *benzenedicarboxylic acids: Phthalic acid, Isophthalic acid* and *Terephthalic acid,* which are formed from benzene by the displacement of two hydrogen atoms by two of the monad groups (CO.OH), because the constitution of these compounds first came under discussion. Phthalic acid is obtained by the oxidation of naphthalene, $C_{10}H_8$, and as Graebe's researches have shown that this hydrocarbon may be regarded as composed of two benzene-nuclei having two atoms of carbon in common; and as, moreover, he considered that these two atoms common to the two nuclei were contiguous, he was necessarily led to the conclusion that the carboxyl groups in phthalic acid were also contiguous, and graphically represented naphthalene and phthalic acid by the following diagrams:


Naphthalene.


Phthalic acid.

This conclusion as to the constitution of phthalic acid was strengthened by the observation that phthalic acid is readily converted into *phthalic anhydride,* $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}O$, whilst the isomeric acids do not yield anhydrides, it being supposed that contiguity of the carboxyl groups, if not absolutely essential, was at least likely to favour the formation of an anhydride.

Isophthalic acid is formed by the oxidation of the modification of *dimethylbenzene* known as *isoxylene,* and this latter is obtained by distilling a mixture of calcic hydrate with the so-called *mesitylenic acid,* $C_6H_3(CH_3)_2.COOH$, formed by oxidation of *mesitylene.* Mesitylene is a *trimethylbenzene* which is obtained from acetone, $CH_3.CO.CH_3$, by the action of sulphuric acid; 3 molecules of acetone losing the elements of 3 molecules of water, and uniting to form a molecule of mesitylene:

$$3C_3H_6O = C_9H_{12} + 3OH_2.$$

Baeyer pointed out that if it be supposed that two atoms of hydrogen are split off from one of the methyl groups of each molecule of acetone together with oxygen, and that the residues coalesce, a trimethylbenzene would be formed in which the three methyl-groups are symmetrically disposed, thus:

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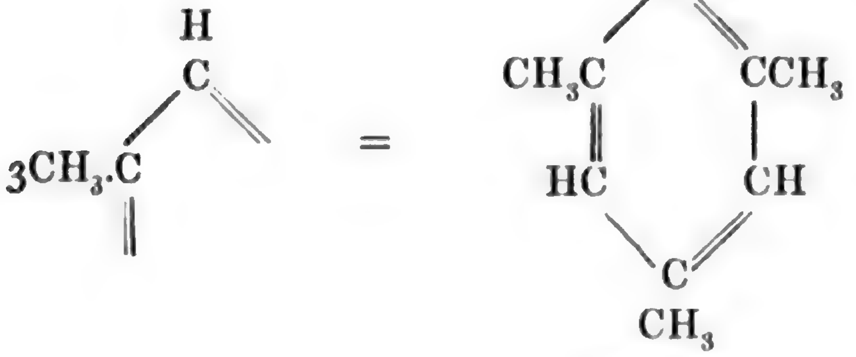
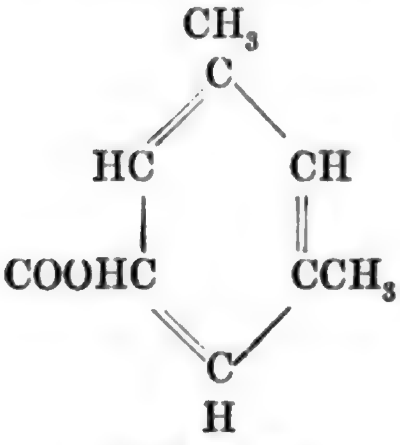
(a) $$\underset{\text{Acetone.}}{CH_3.CO.CH_3} - OH_2 = CH_3.\overset{\|}{C}.\overset{\|}{C}H.$$

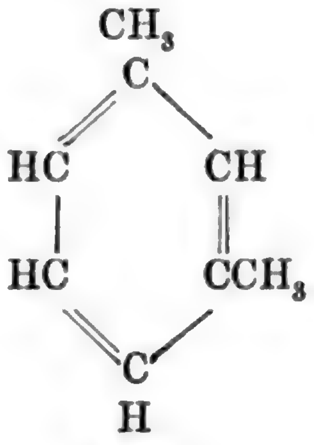
(β)


Mesitylene.

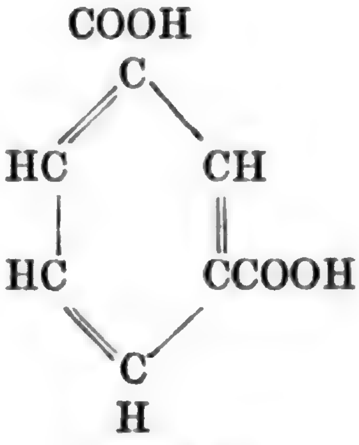
If this hypothesis be correct it will readily be seen that whichever of these methyl-groups is oxidized to carboxyl, a dimethylbenzenecarboxylic acid must be obtained in which the methyl-groups are relatively in the position 1 : 3. The dimethylbenzene obtained from this acid must also have the same constitution, and on oxidation will yield an acid in which the carboxyl-groups are in the position 1 : 3, thus:



Mesitylenic acid.

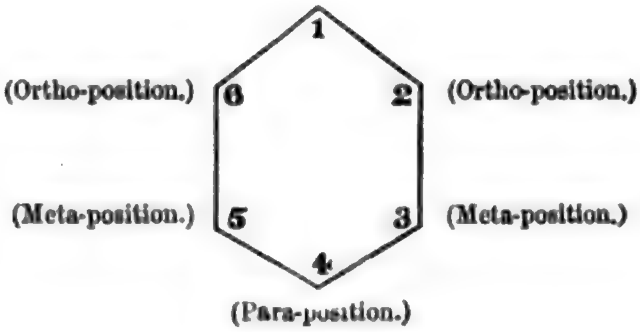


Isoxylene.

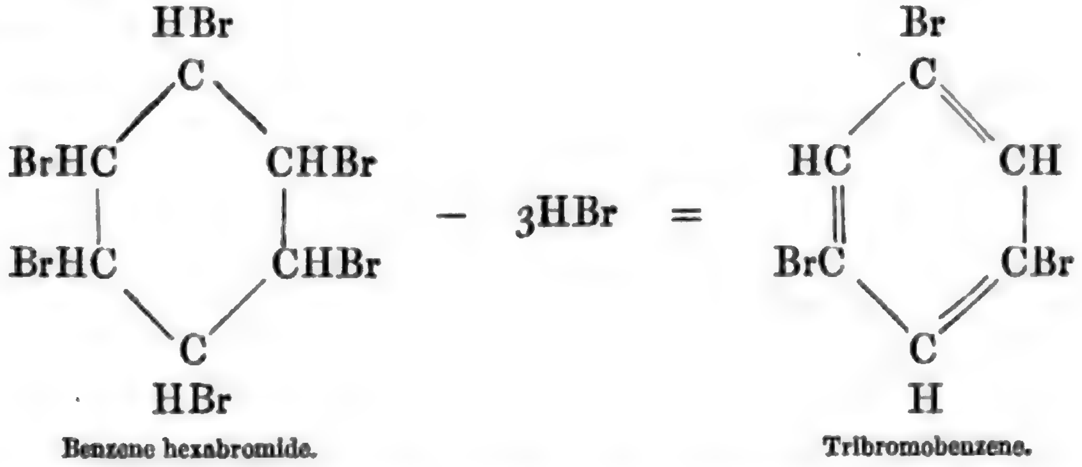


Isophthalic acid.

The position of the carboxyl-groups in phthalic acid being 1 : 2, and in isophthalic acid 1 : 3, it necessarily follows that in terephthalic acid they are as 1 : 4. All di-derivatives of benzene which belong to the same group as phthalic acid may then be supposed to have the substituting radicles in the position 1 : 2; those which belong to the isophthalic group in the position 1 : 3; and finally those which belong to the terephthalic group in the position 1 : 4. Chemists are now very generally agreed in assigning the arbitrary prefix *ortho* to the 1 : 2 derivatives; to the 1 : 3 derivatives the term *meta;* whilst the 1 : 4 derivatives are called *para*-derivatives, although up to within a recent period these terms have been very indiscriminately employed. It is very convenient also, in describing the constitution of the benzene derivatives, to speak of the positions 2 and 6 as the *ortho*-positions; the positions 3 and 5 as the *meta*-positions; and the position 4 as the *para*-position: it being understood that this is relatively to the position 1.

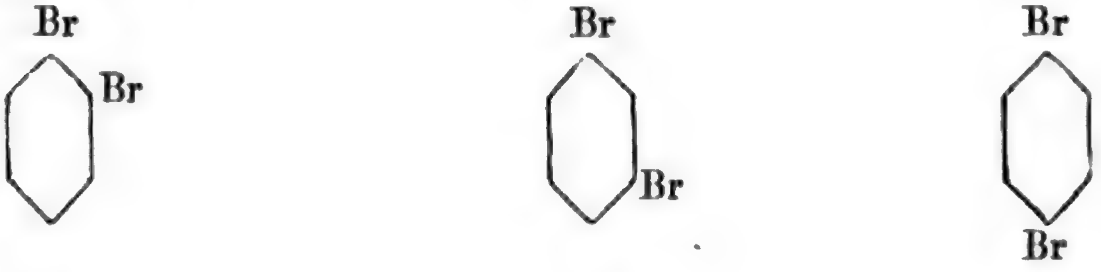


Körner has recently raised an objection to the hypothesis on which the determination of the constitution of phthalic acid rests: that the proof does not hold good unless we assume that the two atoms of carbon in naphthalene common to the two benzene-nuclei are contiguous. There is no cogent reason why these should not be regarded as occupying the relative position 1 : 3, or 1 : 4, and if such were the case phthalic acid would have a different constitution to that assigned to it by Graebe. He has also pointed out that the inference that mesitylene is a symmetrically constituted trimethylbenzene is scarcely admissible, since the application of a similar process of reasoning in a perfectly parallel case leads to a conclusion which is known to be false. Thus, when benzene hexabromide $C_6H_6Br_6$, is treated with potassic hydrate, it is very readily resolved into a tribromobenzene, $C_6H_3Br_3$. There can be no doubt that the six atoms of bromine in the hexabromide are symmetrically distributed, and adopting a similar hypothesis to that of Baeyer, it would appear most probable that the three molecules of hydrobromic acid are removed in such a manner as to furnish a symmetrical tribromobenzene; thus:



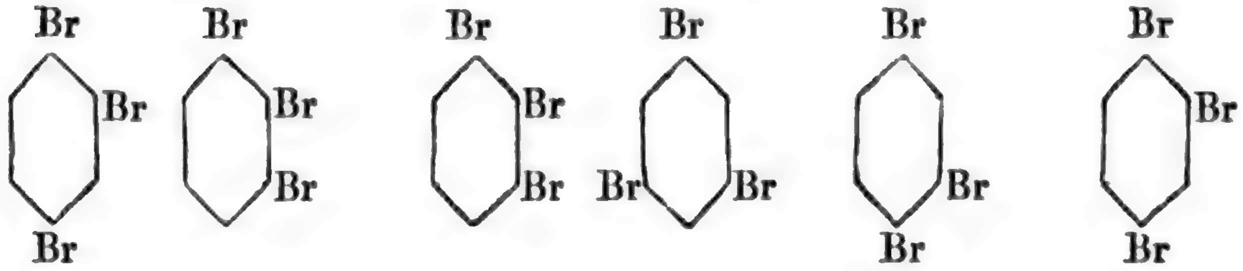
Körner has shown, however, that the tribromobenzene which is formed has the bromine atoms relatively in the positions 1 : 2 : 4. It is therefore not impossible that, in the formation of mesitylene from acetone, isomeric change may have occurred, especially as the reaction takes place at a comparatively high temperature, and under the influence of an extremely powerful reagent.

In face of these very legitimate objections, Körner has sought to determine the constitution of the di-derivatives of benzene entirely without the aid of substances containing a greater number of carbon atoms than benzene. The method which he has employed is to convert the three isomeric dibromobenzenes into tribromobenzenes. The six atoms of hydrogen in benzene being of equal value, only *three* isomeric modifications of tribromobenzene can exist—namely, 1 : 2 : 3, 1 : 2 : 4, and 1 : 3 : 5, but as will be evident on inspection of the accompanying figures, the modification of dibromobenzene in which the bromine atoms are in the position 1 : 2 may give rise to the formation of *two* of the three possible tribromobenzenes; the modification 1 : 3 can, however, furnish *three* tribromobenzenes; whilst only *one* tribromobenzene can be obtained from the modification 1 : 4:



1 : 2 1 : 3 1 : 4

Dibromobenzenes.



1 : 2 : 4 1 : 2 : 3 1 : 2 : 3 1 : 3 : 5 1 : 3 : 4 or 1 : 2 : 4 1 : 2 : 4

Tribromobenzenes.

Or in other words, one of the tribromobenzenes (the modification 1 : 3 : 5) can only be obtained from the 1 : 3 modification of dibromobenzene; whereas a second tribromobenzene (1 : 2 : 3) can be obtained from the 1 : 2 and 1 : 3 modifications of dibromobenzene, and the third tribromobenzene (1 : 2 : 4) can be obtained from each of the three modifications of dibromobenzene. Körner finds that the tribromobenzene from benzene hexabromide can be formed from each of the three dibromobenzenes, and concludes therefore that it has the constitution 1 : 2 : 4; the tribromobenzene obtained by displacing the NH_2 group in ordinary tribromaniline, $C_6H_2Br_3.NH_2$, by hydrogen is only procurable from one of the dibromobenzenes, and the conclusion is obvious that it has the constitution 1 : 3 : 5, and that the dibromobenzene from which it may be derived is 1 : 3; the third tribromobenzene can be prepared from two of the dibromobenzenes, and its constitution is therefore 1 : 2 : 3, and since it is known which of these dibromobenzenes is the 1 : 3 modification, it follows that the other is the 1 : 2, and also that the remaining dibromobenzene is the 1 : 4 modification.

The 1 : 4 modification, or *para*-dibromobenzene, is the crystalline dibromobenzene produced by the action of bromine on benzene; the 1 : 3 modification, or *meta*-dibromobenzene, is formed by displacing the NH_2 group in ordinary dibromaniline, $C_6H_3Br_2.NH_2$, by hydrogen, and is liquid; the 1 : 2 modification, or *ortho*-dibromobenzene, which is also liquid, is formed in small quantity together with paradibromobenzene by the action of bromine on benzene.

On displacing the bromine in paradibromobenzene by methyl, by the action of methyl iodide and sodium:

$$\underset{\text{Paradibromobenzene.}}{C_6H_4Br_2} + 2CH_3I + 4Na = \underset{\text{Paradimethylbenzene.}}{C_6H_4(CH_3)_2} + 2NaI + 2NaBr,$$

and oxidizing the resulting dimethylbenzene, *terephthalic acid* is obtained. Similarly, metadibromobenzene furnishes the ethylic ether of *isophthalic acid* when acted upon with ethylic chlorocarbonate and sodium:

$$\underset{\text{Metadibromobenzene.}}{C_6H_4Br_2} + 2ClCO.OC_2H_5 + 4Na = \underset{\text{Ethylic isophthalate.}}{C_6H_4(CO.OC_2H_5)_2} + 2NaBr + 2NaCl.$$

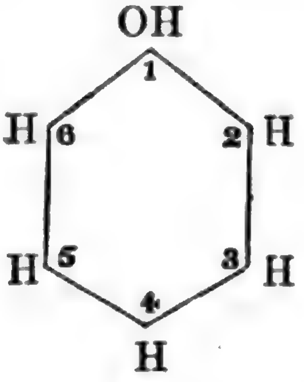
Körner's researches therefore confirm the previous conclusions as to the constitution of the benzenedicarboxylic acids.

With regard to the number of isomeric modifications of the higher substitution derivatives of benzene, it has already been pointed out that only *three* tri-derivatives can exist, supposing the substituting radicles to be the same; but if two different radicles are introduced, no less than *six* modifications are possible: for example, theoretically only *one* nitrodibromobenzene can be obtained from paradibromobenzene, but orthodibromobenzene can furnish *two* and metadibromobenzene *three* nitrodibromobenzenes, viz.:

Paradibromobenzene	Br : Br 1 : 4	Nitroparadibromobenzene	Br : NO_2 : Br 1 : 2 : 4
Metadibromobenzene	Br : Br 1 : 3	Nitrometadibromobenzene.	*a* 1 : 2 : 3 Br : Br : NO_2 *b* 1 : 3 : 4 *c* 1 : 3 : 5
Orthodibromobenzene	Br : Br 1 : 2	Nitrorthodibromobenzene	*a* 1 : 2 : 3 *b* 1 : 2 : 4

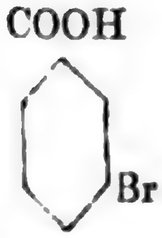
When three dissimilar radicles are introduced, however, no less than *ten* isomeric modifications become possible. In the case of the tetra-derivatives, when all the radicles are the same, only *three* modifications can be produced—viz., 1 : 2 : 3 : 4, 1 : 2 : 4 : 5, and 1 : 3 : 4 : 5; but when two or more dissimilar radicles are present, a far greater number of isomerides are possible. Isomeric penta- and hexa-derivatives of benzene cannot exist according to Kekulé's hypothesis.

Experimental Evidence of the Constitution of Benzene.—Kekulé's hypothesis involves the assumption that the six atoms of hydrogen in benzene are of equal value; but, supposing one of them to be displaced, the remaining five are of different value relatively to the radicle introduced: of these five, two pairs bear respectively similar relations to the radicle, whilst there is no second atom of hydrogen corresponding with the fifth (that in the so-called para-position). Thus, on inspection of the following figure representing phenol, $C_6H_5.OH$, it will be seen that the pair of hydrogen atoms marked 2 and 6 are similarly situated as regards the OH group, and that a second pair exists (3 and 5) also similarly related to the OH group, although the relation of the first and second pairs to the OH group is different:

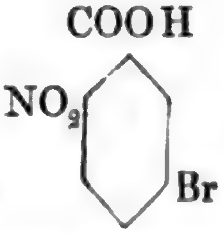


Recent researches show, moreover, that these assumptions are strictly in accordance with facts. It has already been mentioned that the existence of isomeric mono-derivatives of benzene has never been demonstrated, but it is of especial importance to note that all direct attempts to prepare them have failed. Thus Huebner and Alsberg (*Ann. Chem. Pharm.*, clvi. 308) have shown that both the bromonitrobenzenes, $C_6H_4Br.NO_2$, obtained by the action of nitric acid on bromobenzene, C_6H_5Br, yield the same amidobenzene or aniline, $C_6H_5.NH_2$, when they are reduced to bromanilines, and the bromine is displaced by hydrogen; and that this aniline is identical with that from *nitrobenzene*, $C_6H_5.NO_2$. Even if, as is probable, the same atom of hydrogen in benzene is displaced, whether it be acted on with bromine or nitric acid, there can be no doubt that different atoms of hydrogen are displaced by the NO_2 group in the formation of nitrobenzene, and of the two nitrobromobenzenes from bromobenzene; but as the anilines from these three sources are identical, it may be concluded with certainty that at least three of the hydrogen atoms in benzene are of the same value, and that the others also probably are, since it is extremely unlikely according to our experience that, if this were not the case, identical substances would be obtained in the three instances above described; thus it will be recollected that in the case of the normal paraffins, in which we regard the hydrogen atoms as not all relatively of the same value, isomeric monochlorinated derivatives are obtained by the action of chlorine (p. 149).

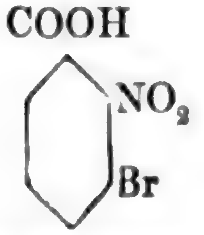
The following experiments may be regarded as affording decisive proof of the existence of pairs of hydrogen atoms of equal value. According to Huebner and Petermann (*ibid.* cxlix. 129), when metabromobenzoic acid is nitrated, *two isomeric orthonitrometabromobenzoic acids are obtained both of which yield orthamidobenzoic acid on reduction,* thus proving that two of the atoms of hydrogen in benzoic acid are symmetrically situated relatively to the COOH group, and that therefore in the language of Kekulé's hypothesis, the positions 1 : 2 and 1 : 6 are identical. This will perhaps be better understood on reference to the following figures:



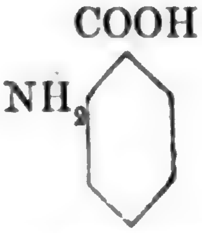
Metabromobenzoic acid.



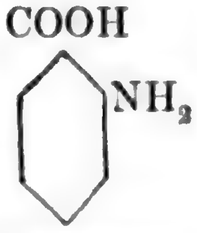
α-Nitrometabromobenzoic acid.



β-Nitrometabromobenzoic acid.

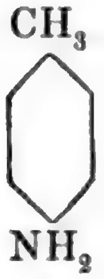


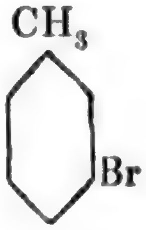
Orthamidobenzoic acid from α-Nitro-acid.

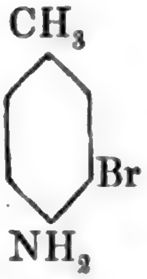


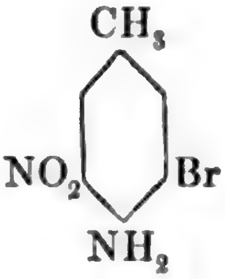
Orthamidobenzoic acid from β-Nitro-acid.

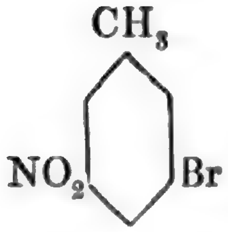
A proof of the existence of a second pair of similarly related hydrogen atoms is given by Wroblevsky's recent experiments (*Deut. chem. Ges. Ber.*, viii. 573). He has shown that by the action of bromine on the acetyl-derivative of paramidotoluene (Fig. I. p. 272), the corresponding derivative of a bromoparamidotoluene is obtained, which furnishes *metabromotoluene* (Fig. II.), when the amido-group, NH_2, is displaced by hydrogen. Starting with this metabromoparamidotoluene (Fig. III.), he has successively converted it into nitrobromamidotoluene (Fig. IV.), nitrobromotoluene (Fig. V.), amidobromotoluene (Fig. VI.), and amidotoluene (Fig. VII.); the amidotoluene thus produced was found to be *metamidotoluene,* and to furnish *metabromotoluene* (Fig. VIII.), when bromine was introduced in place of the NH_2 group. The course of this somewhat complex series of reactions, and the nature of the proof of the existence of the meta-position twice which it affords, will be evident on inspection of the following figures:

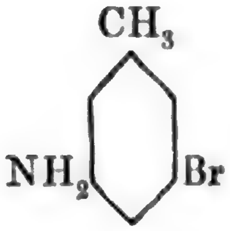

I.

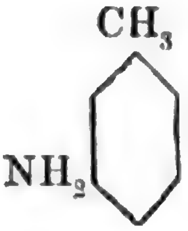

II.

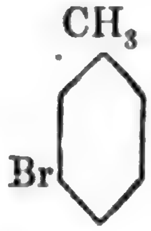

III.


IV.


V.


VI.


VII.


VIII.

The existence of two pairs of atoms of hydrogen respectively of equal value as regards the radicle in any given mono-derivative of benzene having been experimentally demonstrated, it may also be proved by experimental evidence, as Ladenburg has shown (*ibid.* vii. 1684), that the six atoms of hydrogen in benzene are of equal value. The proof in question is based on the following propositions:

1. The carboxyl-group in benzoic acid, $C_6H_5.COOH$, displaces the same hydrogen atom, *a*, as the hydroxyl-group in phenol, $C_6H_5.OH$, since phenol may be converted by the action of phosphoric bromide into bromobenzene, C_6H_5Br, which furnishes benzoic acid on treatment with carbonic anhydride and sodium:

$$\underset{\text{Bromobenzene.}}{C_6H_5Br} + 2Na + CO_2 = \underset{\text{Sodic benzoate.}}{C_6H_5.COONa} + NaBr.$$

2. In the three oxybenzoic acids, $C_6H_4.OH.COOH$, the OH group displaces three hydrogen atoms, *b*, *c*, and *d*, different from *a* and from each other. No other reasonable explanation of the isomerism amongst the three acids in question can be given than by supposing that the OH group in them displaces three hydrogen atoms, *b*, *c* and *d*, differently placed relatively to *a*, and Beilstein has shown that the benzoic acid obtained by displacing the OH group in salicylic and paraoxybenzoic acid by hydrogen is identical with ordinary benzoic acid; hence there can be no doubt

that in these acids the carboxyl group displaces the hydrogen atom *a*. We may infer that this is also the case with oxybenzoic acid, from the fact that it can be procured from benzoic acid by a variety of methods.

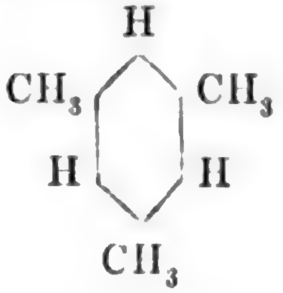
3. The phenols from the three oxybenzoic acids are identical amongst themselves and with ordinary phenol; hence the four atoms of hydrogen, *a, b, c,* and *d,* in benzene are of equal value. Ladenburg has himself proved, by carefully comparing the phenols from the several sources, that they are identical.

4. Since the three atoms of hydrogen, *b, c,* and *d,* in benzoic acid cannot be symmetrically situated with reference to the carboxyl group which has displaced *a,* (inasmuch as otherwise three isomeric oxybenzoic acids could not be obtained by their displacement by OH,) and it has been proved that there are two symmetrical pairs of hydrogen atoms in any given mono-derivative of benzene, it follows that there are two atoms of hydrogen, *e* and *f,* by the displacement of which by OH, oxybenzoic acids must be obtained identical with those already known. But according to Huebner and Petermann's and Wroblevsky's experiments, the acids which would be thus formed are salicylic and oxybenzoic acids, and these, it need scarcely be said, would yield phenols identical with those previously obtained. It can thus be shown that we may displace each of the six atoms of hydrogen in benzene by OH, and yet always obtain the same phenol: hence only one phenol can exist, and moreover the six atoms of hydrogen in benzene are of equal value.

Ladenburg has also recently shown beyond question that mesitylene is a symmetrically constituted trimethylbenzene. The six atoms of hydrogen in benzene being of equal value, if three are displaced by methyl it will be a matter of indifference which of the remaining three are displaced by any given radicle if they are symmetrically related to the three methyl-groups; but if this be not the case, we may expect the formation of isomeric substitution derivatives of mesitylene. Ladenburg, therefore, instituted the following series of experiments:—*Dinitromesitylene,* $C_9H_{10}(NO_2)_2$, prepared by the action of nitric acid on mesitylene, was reduced to *amidonitromesitylene,* $C_9H_{10}(NO_2)(NH_2)$, and the acetyl-derivative of the latter converted by nitration into *acetamidodinitromesitylene;* the *amidodinitromesitylene,* $C_9H_9(NO_2)_2(NH_2)$, separated from this compound was found to be identical with that obtained by reducing *trinitromesitylene,* $C_9H_9(NO_2)_3$, and to furnish dinitromesitylene *identical* with that prepared directly from mesitylene, when the NH_2 group was displaced by hydrogen.

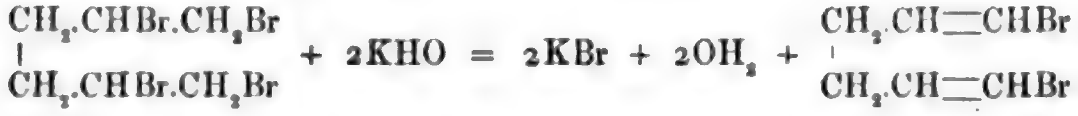
Furthermore, the *nitromesitylenes*, $C_9H_{11}.NO_2$, obtained by nitrating mesitylene, and by displacing the NH_2 group in amidonitromesitylene by hydrogen, were proved to be *identical*, and by nitrating the acetyl-derivative of *amidomesitylene*, $C_9H_{11}.NH_2$, from nitromesitylene, the acetyl-derivative of an amidonitromesitylene was obtained, *identical* with that from dinitromesitylene.

If we suppose that the atoms of hydrogen, which we may call *a* and *b*, are displaced by the NO_2 group in the dinitromesitylene directly prepared from mesitylene, and that the NO_2 group which displaces *b* is that which is reduced to NH_2 in the formation of amidonitromesitylene, it then follows that in the amidodinitromesitylene and dinitromesitylene obtained from amidonitromesitylene, the NO_2 group displaces the hydrogen atom *a*, and a third atom, which may be called *c*. This being the case, the fact that the nitromesitylene from mesitylene is identical with that from amidonitromesitylene proves that the hydrogen atoms *b* and *c* are of equal value, because *a* being displaced by NO_2, the same dinitromesitylene is obtained as when a second NO_2 group is introduced in place of either *b* or *c*. Moreover, as we have supposed that in nitromesitylene from dinitromesitylene the NO_2 group has displaced the hydrogen atom *a*, if in that directly prepared from mesitylene the NO_2 group had displaced *b* or *c*, the identity of the nitromesitylene from the two sources would at once prove that the hydrogen atoms *a b* and *a c* respectively are of equal value. But even if the NO_2 group, in the nitromesitylene prepared directly from mesitylene, also have displaced *a*, the NH_2 group in the amidonitromesitylene formed from it would have displaced *a* also, and the NO_2 group consequently would have displaced *b* or *c*. Since, however, this amidonitromesitylene, *a b* or *a c*, is identical with that, *a b*, from dinitromesitylene, it follows that the three atoms of hydrogen in mesitylene belonging to the benzene-nucleus are of equal value, or in other words, that they are symmetrically related to the three methyl groups. Consequently the methyl groups in mesitylene are also symmetrically placed, and the only formula which, according to Kekulé's hypothesis, harmonizes with this conclusion is that already given, viz.:



It will be evident, also, that Ladenburg's experiments afford a further proof that in the *meta*-di-derivatives the radicles are in the position 1 : 3.

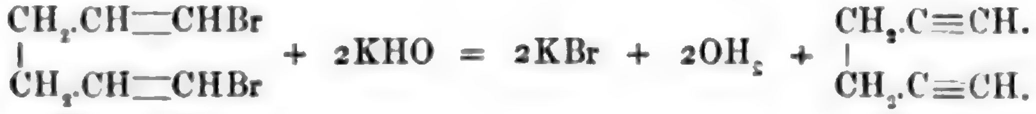
(1293) Dipropargyl : C_6H_6 or $HC \equiv C.CH_2.CH_2.C \equiv CH$.—This hydrocarbon is isomeric with benzene, from which, however, it differs very widely. To prepare it, the tetrabromohexane from diallyl or diallyl tetrabromide (1255) is distilled with a considerable excess of solid potassic or sodic hydrate; the elements of two molecules of hydrobromic acid are thus removed, and a ***dibromodiallyl*** is produced.



$$\begin{array}{l} CH_2.CHBr.CH_2Br \\ | \\ CH_2.CHBr.CH_2Br \end{array} + 2KHO = 2KBr + 2OH_2 + \begin{array}{l} CH_2.CH = CHBr \\ | \\ CH_2.CH = CHBr \end{array}$$

Diallyl tetrabromide. Dibromodiallyl.

When this dibromodiallyl is digested with an excess of a concentrated alcoholic solution of potassic hydrate, the elements of two molecules more of hydrobromic acid are eliminated, and dipropargyl is formed :



$$\begin{array}{l} CH_2.CH = CHBr \\ | \\ CH_2.CH = CHBr \end{array} + 2KHO = 2KBr + 2OH_2 + \begin{array}{l} CH_2.C \equiv CH. \\ | \\ CH_2.C \equiv CH. \end{array}$$

Dibromodiallyl. Dipropargyl.

Dipropargyl is a mobile, colourless, highly refractive liquid, having a peculiar and most penetrating odour. It boils at about 85° (185° F.), and at 18° (64°·4 F.) has the specific gravity ·81. It burns with a luminous smoky flame. It is insoluble in water. When added to an ammoniacal solution of cuprous chloride, dipropargyl produces a greenish-yellow precipitate, which, when dried over sulphuric acid, or at 90°—100° (194°—212° F.), has the composition $C_6H_4(Cu_2) + 2OH_2$. This compound explodes at about 100° (212° F.) In an aqueous solution of argentic nitrate it produces a white amorphous precipitate, $C_6H_4Ag_2 + 2OH_2$, which, on exposure to light, soon becomes pink, and then black; in the dry state, this substance explodes readily at a temperature far below 100° (212° F.). These metallic derivatives furnish dipropargyl when treated with dilute mineral acids.

When bromine is added to dipropargyl, combination takes place with extreme violence, and the *tetrabromide*, $C_6H_6Br_4$, is produced; it is a viscid liquid, of the specific gravity 2·64 at 19° (66°·2 F.), insoluble in water, but soluble in alcohol and ether. It is decomposed when heated, hydrobromic acid being given off, and a carbonaceous mass remaining. Dipropargyl tetrabromide slowly combines with bromine in the cold, and rapidly when the mixture is carefully heated, forming *dipropargyl-octobromide*, $C_6H_6Br_8$. The octobromide separates from ether as a brilliant white crystalline powder, but by spontaneous evaporation of its solution in carbonic bisulphide, distinct rhombohedrons of considerable size may be obtained. It melts at 140°—141° (284°—285°·8 F.), but is not volatile. (Henry, *Deut. chem. Ges. Ber.*, vi. 955; vii. 20.)

(1294) HOMOLOGUES OF BENZENE.—These are formed from benzene by the displacement of one or more atoms of hydrogen by the so-called radicles of the series C_nH_{2n+1}. Up to the present time, however, no more than four atoms of hydrogen have been thus displaced, and no radicle higher than hexyl, C_6H_{13}, has been introduced into benzene. The homologues of benzene may be prepared in the following manner:

1. By the action of sodium on a mixture of a bromo- or iodoparaffin with bromobenzene; this method gives rise to the formation of hydrocarbons of the form $C_6H_5.C_nH_{2n+1}$:

$$C_6H_5Br + C_nH_{2n+1}I + 2Na = C_6H_5.C_nH_{2n+1} + NaI + NaBr.$$

$$\underset{\text{Bromobenzene.}}{C_6H_5Br} + CH_3I + 2Na = \underset{\text{Methylbenzene.}}{C_6H_5.CH_3} + NaI + NaBr.$$

By similarly treating the monobromo-derivatives of the hydrocarbons of the form $C_6H_5.C_nH_{2n+1}$, hydrocarbons of the series $C_6H_4(C_nH_{2n+1})_2$ are produced, and from the monobromo-derivatives of these hydrocarbons others of the form $C_6H_3(C_nH_{2n+1})_3$ may be obtained:

$$C_6H_4Br.C_nH_{2n+1} + C_nH_{2n+1}I + 2Na = C_6H_4(C_nH_{2n+1})_2 + NaI + NaBr.$$

$$\underset{\text{Bromomethylbenzene.}}{C_6H_4Br.CH_3} + CH_3I + 2Na = \underset{\text{Dimethylbenzene.}}{C_6H_4(CH_3)_2} + NaBr + NaI.$$

$$C_6H_3Br(C_nH_{2n+1})_2 + C_nH_{2n+1}I = C_6H_3(C_nH_{2n+1})_3 + NaBr + NaI.$$

$$\underset{\text{Bromodimethylbenzene.}}{C_6H_3Br(CH_3)_2} + CH_3I + 2Na = \underset{\text{Trimethylbenzene.}}{C_6H_3(CH_3)_3} + NaI + NaBr.$$

When several C_nH_{2n+1} radicles are in this way introduced into benzene, it is not necessary that they should all be the same; thus by treating a mixture of bromomethylbenzene and ethylic bromide with sodium, an ethylmethylbenzene is produced. Moreover, although the attempt has not been made to introduce more than *two* different radicles into benzene, there can be little doubt that if the bromo-derivative of ethylmethylbenzene, for example, were acted on with propylic iodide, C_3H_7I, and sodium, a propylethylmethylbenzene could be obtained. By employing isomeric bromo-derivatives, isomeric hydrocarbons may be produced: thus three isomeric bromomethylbenzenes are known, and from these, by treatment with sodium and methylic iodide, three isomeric dimethylbenzenes have been prepared.

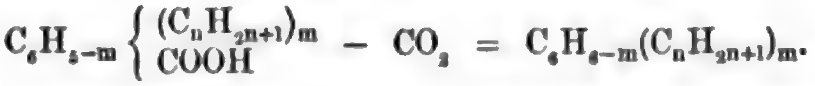
The *mono*bromo-derivatives of benzene and its homologues have been almost exclusively employed in the synthetical preparation of the hydrocarbons of the benzene series in the manner above described; the only exceptions are the conversion of paradibromobenzene into paradimethylbenzene, and of dibromotoluene into pseudocumene, by the action of sodium and methylic iodide.

It is always necessary to dilute the mixture of haloid derivatives before acting on it with sodium, in order to moderate the violence of the reaction; about an equal volume of dry ether free from alcohol is therefore usually added, but in some cases pure dry benzene is advantageously employed as the diluent.

2. By acting on a mixture of the so-called benzylic chloride with amylic bromide and sodium a *hexylbenzene* is obtained, and doubtless this method will prove to be of general application for the preparation of hydrocarbons of the form $C_6H_5.CH_2.C_nH_{2n+1}$:

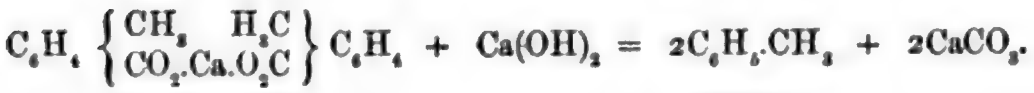
$$\underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} + \underset{\text{Amylic bromide.}}{C_5H_{11}Br} + 2Na = \underset{\text{Hexylbenzene.}}{C_6H_5.CH_2.C_5H_{11}} + NaBr + NaCl.$$

3. A method which is also general consists in carefully distilling the calcic salts of the acids of the benzoic series, or the acids themselves, with calcic hydrate, whereby the elements of a molecule of carbonic anhydride are removed:*



$$C_6H_{5-m}\left\{\begin{matrix}(C_nH_{2n+1})_m\\ COOH\end{matrix}\right. - CO_2 = C_6H_{6-m}(C_nH_{2n+1})_m.$$

Acid of Benzoic series. Hydrocarbon of the Benzene series.



$$C_6H_4\left\{\begin{matrix}CH_3 \quad H_3C\\ CO_2.Ca.O_2C\end{matrix}\right\}C_6H_4 + Ca(OH)_2 = 2C_6H_5.CH_3 + 2CaCO_3.$$

Calcic Toluate. Toluene.

4. When a mixture of acetone or dimethyl ketone with sul-

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* Fittig (*Ann. Chem. Pharm.*, cxlviii. 2) recommends that the acid be intimately mixed with about three times its weight of burnt lime, and the mixture introduced into a flask, at the bottom of which a thin layer of lime has previously been placed. A thin layer of lime is also put on top of the mixture. At most 20—30 grms. of the acid should be taken at a time. The flask, attached to a condenser, is suspended by the neck in the centre of a roomy charcoal stove, which is preferable to a gas flame, since it is possible with it to heat the flask on all sides equally, and to avoid overheating it.

phuric acid is carefully distilled, the modification of trimethylbenzene, known as mesitylene is obtained:

$$\underset{\text{Dimethylketone.}}{3CH_3.CO.CH_3} - 3OH_2 = \underset{\text{Mesitylene.}}{C_6H_3(CH_3)_3}.$$

In like manner, homologues of mesitylene may be prepared from the ketones of the form $CH_3.CO.C_nH_{2n+1}$:

$$3C_nH_{2n+1}.CO.CH_3 - 3OH_2 = C_6H_3(C_nH_{2n+1})_3.$$

5. Hydrocarbons of the benzene series are also produced in various special reactions, which will be described as occasion offers.

The following is a complete list of the hydrocarbons of this series as far as they are at present known :—

			B. P. Cent. °
C_6H_6	Benzene	C_6H_6	81
C_7H_8	Methylbenzene (toluene) . . .	$C_6H_5(CH_3)$	111
C_8H_{10}	Ethylbenzene	$C_6H_5(C_2H_5)$	134
	Dimethylbenzenes (xylenes):		
	Paradimethylbenzene	$C_6H_4(CH_3)_2$	136—137
	Metadimethylbenzene	$C_6H_4(CH_3)_2$	137—137·5
	Orthodimethylbenzene	$C_6H_4(CH_3)_2$	140—141
C_9H_{12}	Propylbenzene	$C_6H_5(C_3H_7)^{\alpha}$	157
	Isopropylbenzene (cumene) . . .	$C_6H_5(C_3H_7)^{\beta}$	151
	Parethylmethylbenzene	$C_6H_4(CH_3)(C_2H_5)$	161—162
	Trimethylbenzenes:		
	(1 : 3 : 5) Mesitylene	$C_6H_3(CH_3)_3$	163
	(1 : 3 : 4) Pseudocumene . . .	$C_6H_3(CH_3)_3$	166—167
$C_{10}H_{14}$	β-Butylbenzene	$C_6H_5(C_4H_9)^{\beta}$	159—161
	Parapropylmethylbenzene (cymene).	$C_6H_4(CH_3)(C_3H_7)^{\alpha}$	178—179
	Paradiethylbenzene	$C_6H_4(C_2H_5)_2$	178—179
	(1 : 3 : 4) Ethyldimethylbenzene .	$C_6H_3(C_2H_5)(CH_3)_2$	183—184
	(1 : 3 : 5) Ethyldimethylbenzene .	$C_6H_3(C_2H_5)(CH_3)_2$	180—182
	(1 : 2 : 3 : 5) Tetramethylbenzene .	$C_6H_2(CH_3)_4$	192—194
	Tetramethylbenzene (durene) . .	$C_6H_2(CH_3)_4$	189—191
$C_{11}H_{16}$	β-Amylbenzene	$C_6H_5(C_5H_{11})^{\beta}$	193
	θ-Amylbenzene	$C_6H_5.CH(C_2H_5)_2$	175—180
	(1 : 3 : 5) Propyldimethylbenzene .	$C_6H_3(C_3H_7)(CH_3)_2$	206—210
	Laurene (? propyldimethylbenzene) .	$C_6H_3(CH_3)_2(C_3H_7)^{\beta}$	188
	(1 : 3 : 5) Diethylmethylbenzene .	$C_6H_3(CH_3)(C_2H_5)_2$	198—200
$C_{12}H_{18}$	β-Hexylbenzene	$C_6H_5(C_6H_{13})^{\beta}$	214—215
	β-Amylmethylbenzene	$C_6H_4(CH_3)(C_5H_{11})^{\beta}$	213
	(1 : 3 : 5) Triethylbenzene . . .	$C_6H_3(C_2H_5)_3$	217—220
$C_{13}H_{20}$	β-Amyldimethylbenzene	$C_6H_3(CH_3)_2(C_5H_{11})^{\beta}$	232—233
	(1 : 3 : 5) Methyldipropylbenzene .	$C_6H_3(CH_3)(C_3H_7)_2$	243—248

(1295) *Behaviour of the Homologues of Benzene on Oxidation.*—The behaviour of the homologues of benzene on oxidation is especially characteristic. When the hydrocarbons formed from benzene by the introduction of a single C_nH_{2n+1} radicle, or side chain, as it is often termed, are oxidized, the *monobasic* acid, *benzoic acid*, is always produced; thus:

$$\underset{\text{Methylbenzene.}}{C_6H_5.CH_3} + 3O = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + OH_2.$$

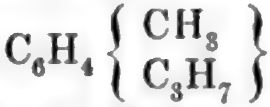
In the case of those derivatives which contain several side chains, however, *polybasic* acids are formed, each of the side chains, whatever its complexity, undergoing oxidation to COOH, which remains in combination with the benzene-nucleus, so that acids are usually obtained containing the same number of COOH groups as there were originally C_nH_{2n+1} groups: paradimethylbenzene, $C_6H_4(CH_3)_2$, for example, furnishes terephthalic acid, $C_6H_4(COOH)_2$, and trimethylbenzene (mesitylene), $C_6H_3(CH_3)_3$, is oxidized to the acid $C_6H_3(COOH)_3$. There can be little doubt that this reaction always takes place, and that in the few instances in which the formation of the acid thus related to the hydrocarbon has not been observed, it is because of its instability under the influence of the oxidizing agent employed; thus the three isomeric dimethylbenzenes furnish the three corresponding methylbenzoic acids, $C_6H_4(CH_3).COOH$, when oxidized with dilute nitric acid, but, on further oxidation with potassic dichromate and sulphuric acid mixture, only two of these acids are converted into the corresponding dibasic phthalic acids, the third (orthomethylbenzoic acid) being completely destroyed. From this circumstance, and as other similar instances of the instability of ortho-derivatives were known, it was long supposed that these compounds were not capable of yielding the corresponding acids; Weith has recently shown, however (*Deut. chem. Ges. Ber.*, vii. 1057), that, when orthomethylbenzoic acid is oxidized with an alkaline solution of potassic permanganate, almost the theoretical quantity of phthalic acid may be obtained.

The oxidation of the hydrocarbons which contain several side chains may take place in several stages, each radicle, in fact, being successively oxidized to COOH, so that as many acids may be obtained from a hydrocarbon of the benzene series as there are side chains in it. Mesitylene, for example, is first oxidized to the monobasic mesitylenic acid, which on further treatment yields the dibasic mesidic or uvitic acid, and this is finally converted into the tribasic trimesic acid:

$$\underset{\text{Mesitylene.}}{C_6H_3(CH_3)_3} + 3O = \underset{\text{Mesitylenic acid.}}{C_6H_3(CH_3)_2.COOH} + OH_2.$$

$$\underset{\text{Mesitylenic acid.}}{C_6H_3(CH_3)_2.COOH} + 3O = \underset{\text{Mesidic acid.}}{C_6H_3(CH_3)(COOH)_2} + OH_2.$$

$$\underset{\text{Mesidic acid.}}{C_6H_3(CH_3)(COOH)_2} + 3O = \underset{\text{Trimesic acid.}}{C_6H_3(COOH)_3} + OH_2.$$

Benzene is obtained on distilling mesitic acid with calcic hydrate, proving that in mesitic acid all the side chains are oxidized; from this it is evident that oxidation affords a most valuable means of determining the constitution of any hydrocarbon of the benzene series. When hydrocarbons containing different radicles are oxidized, the least stable of these, which is usually the most complex, is first attacked; thus propylmethylbenzene or cymene,  $C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}$, furnishes *methylbenzoic acid*, the propyl group being first oxidized to COOH. This result, however, probably depends on the nature of the oxidizing agent employed, since it has been shown (Nencki and Ziegler. *Deut. chem. Ges. Ber.*, v. 749) that when cymene is taken internally either by dogs or human beings, it is oxidized and voided with the urine in the form of *propylbenzoic* or *cumic acid*, $C_6H_4(C_3H_7).COOH$; in this case, therefore, the methyl group is oxidized first, but no similar result has ever been obtained with artificial oxidizing agents.

Our knowledge with regard to the complementary products which are formed by the oxidation of the C_nH_{2n+1} radicle is at present extremely limited, it being only known that propylmethylbenzene furnishes paratoluic and *acetic* acids:

$$\underset{\text{Propylmethylbenzene.}}{C_6H_4\left\{\begin{matrix}CH_3\\CH_2.CH_2.CH_3\end{matrix}\right.} + 5O = \underset{\text{Paratoluic acid.}}{C_6H_4\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.} + \underset{\text{Acetic acid.}}{CH_3.COOH} + OH_2;$$

and that β-amylbenzene yields *isobutyric acid* in addition to benzoic acid:

$$\underset{\beta\text{-Amylbenzene.}}{C_6H_5.CH_2.CH_2.CH(CH_3)_2} + 5O = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + \underset{\text{Isobutyric acid.}}{CH(CH_3)_2.COOH} + OH_2.$$

But from these results, and guided also by analogy, it may be inferred that if the C_nH_{2n+1} radicle be a primary radicle of the form $C_nH_{2n+1}.CH_2$, by its oxidation an acid of the acetic series will be produced containing one atom of carbon less, in the manner indicated by the following general equation:

$$\underset{\text{Hydrocarbon of the Benzene series.}}{C_6H_5(CH_2.C_nH_{2n+1})} + 5O = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + \underset{\text{Acid of the acetic series.}}{C_nH_{2n}O_2} + OH_2.$$

$$\underset{\text{Hydrocarbon of the Benzene series.}}{C_6H_4(CH_2.C_nH_{2n+1})_2} + 10O = \underset{\text{Acid of the Phthalic series.}}{C_6H_4(COOH)_2} + \underset{\text{Acid of the acetic series.}}{2C_nH_{2n}O_2} + 2OH_2.$$

(1296) *Action of Hydrogen on the Homologues of Benzene.*— According to Berthelot, when the hydrocarbons of the benzene series are heated with a saturated solution of hydriodic acid to 280° (536° F.) for 24 hours, they are ultimately converted into the corresponding paraffins. Baeyer has shown (*Deut. chem. Ges. Ber.*, i. 12; ii. 21), however, that dry hydriodic acid* has no action on benzene even at 350° (662° F.), but that methylbenzene takes up *two* atoms of hydrogen, dimethylbenzene four atoms of hydrogen, and trimethylbenzene (mesitylene) six atoms of hydrogen when submitted to its action at the same temperature as that employed by Berthelot. The difference in the results obtained by these two chemists is perhaps attributable to the presence of iodine, when aqueous hydriodic acid is employed.

(1297) *Action of the Halogens on the Homologues of Benzene.*— Additive compounds with chlorine and bromine corresponding with those formed from benzene have not been obtained from the homologues of benzene; they are, however, all readily acted on by chlorine and bromine, but the nature of the products varies considerably according to the conditions under which the action takes place. Thus when chlorine is passed into *cooled* toluene, $C_6H_5.CH_3$, a chlorotoluene is produced which is isomeric with that formed by the action of chlorine on the *boiling* hydrocarbon; the latter being converted by the action of oxidizing agents into *benzoic acid,* $C_6H_5.COOH$, and the former into *chlorobenzoic acid,* $C_6H_4Cl.COOH$. This behaviour shows that in the one case the chlorine has displaced hydrogen in the C_6H_5 group, and in the other in the CH_3 group; the two compounds are therefore represented respectively by the formulæ $C_6H_4Cl.CH_3$ and $C_6H_5.CH_2Cl$. The compound $C_6H_5.CH_2Cl$, which is commonly known as *benzylic chloride,* readily exchanges its chlorine for other radicles: thus when heated with potassic acetate, it is converted into *benzylic acetate,* $C_6H_5.CH_2(C_2H_3O_2)$, which on saponification furnishes *benzylic alcohol,* $C_6H_5.CH_2(OH)$; and in this respect the behaviour of benzylic chloride is completely analogous with that of the mono-haloid derivatives of the paraffins.

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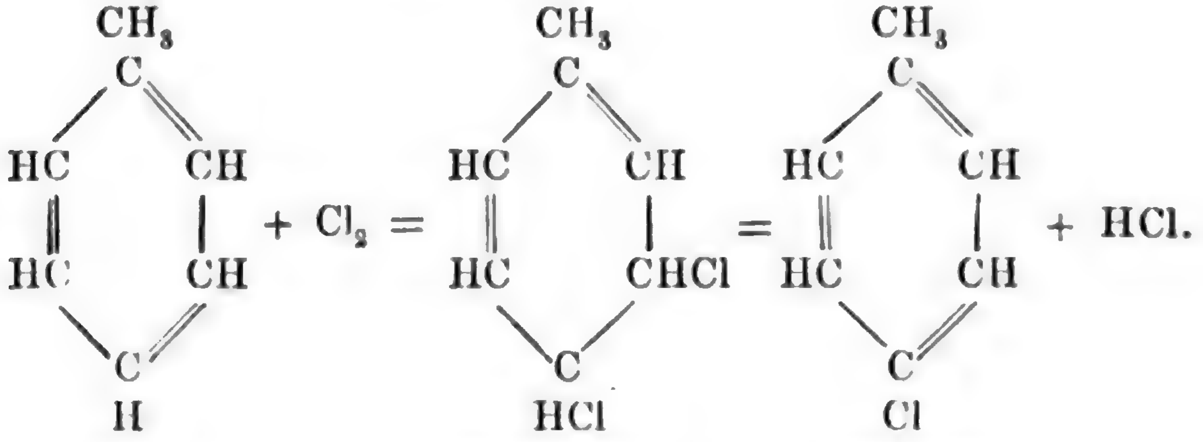
* He employed *phosphonic iodide,* PH_4I, which is decomposed when heated into hydriodic acid and phosphine, PH_3.

The compound $C_6H_4Cl.CH_3$, however, does not enter into reactions of double decomposition, and is a much more stable body than benzylic chloride. Again, if the action of chlorine on toluene takes place in presence of iodine, antimonic pentachloride, or molybdenic pentachloride, chlorotoluene alone is produced even when the toluene is heated to boiling, and by the continued action of chlorine under these circumstances, the five atoms of hydrogen in the C_6H_5 group in toluene may be successively displaced by chlorine, and a series of bodies obtained having properties similar to those of chlorotoluene. On the other hand, when chlorine acts on boiling benzylic chloride the two remaining atoms of hydrogen in the CH_3 group in toluene become displaced, and the compounds $C_6H_5.CHCl_2$ and $C_6H_5.CCl_3$ are formed, which also, like benzylic chloride, readily yield up their chlorine in exchange for other elements. By treating benzylic chloride with chlorine in presence of iodine, or by chlorinating boiling chlorotoluene, the compound $C_6H_4Cl.CH_2Cl$ is formed, which is isomeric with the dichlorotoluene, $C_6H_3Cl_2.CH_3$, obtained by chlorinating toluene in presence of iodine, and the compound $C_6H_5.CHCl_2$, produced by chlorinating boiling benzylic chloride; the compound $C_6H_4Cl.CH_2Cl$ exchanges only one of its atoms of chlorine for other radicles, and is thus intermediate in its behaviour between $C_6H_3Cl_2.CH_3$ and $C_6H_5.CHCl_2$.

The only explanation which can be offered at present of this remarkable difference in the action of chlorine, is that when it acts on *boiling* toluene, hydrogen in the CH_3 group is *directly displaced*, as it is when the paraffins are similarly treated; but that when the action takes place in the cold, or in the presence of any of the above mentioned substances, an additive compound is first produced, which, however, rapidly loses haloid acid and is converted into the chloro-derivative. According to this view, the action of chlorine on toluene at a low temperature may be illustrated by the following diagrams:



Toluene. Toluene dichloride. Chlorotoluene.

The homologues of toluene exhibit a precisely similar behaviour with chlorine. The action of bromine on the homologues of benzene is also similar to that of chlorine; the action of iodine alone, however, does not give rise to the formation of iodo-derivatives. By continuing the action of chlorine in presence of iodine on the homologues of benzene the whole of the hydrogen may be displaced, but these *perchlorinated* derivatives readily break up under the influence of the chlorine in such a manner that *hexachlorobenzene*, C_6Cl_6, is always produced together with the *perchlorinated paraffin*, or its products of decomposition by chlorine, corresponding with the side chain; thus toluene, $C_6H_5.CH_3$, is converted into hexachlorobenzene, C_6Cl_6, and tetrachloromethane, CCl_4, whilst cymene, $C_6H_4(CH_3)(C_3H_7)$, furnishes hexachlorobenzene, tetrachloromethane, and octochloropropane C_3Cl_8 (Krafft and Merz, *Deut. chem. Ges. Ber.*, viii. 1296).

(1298) *Action of Nitric and Sulphuric Acids on the Homologues of Benzene.*—The hydrocarbons of the benzene series are all converted by the action of *concentrated* nitric acid into *nitro*-derivatives, one or more atoms of hydrogen in the benzene nucleus being displaced by the monad NO_2 group; but when the homologues of benzene are boiled with *dilute* nitric acid, they undergo oxidation, the side chains alone being affected.

The action of concentrated sulphuric acid on benzene and its homologues leads to the production of *sulpho-acids*, one or more atoms of hydrogen in the benzene nucleus being displaced by the monad group $SO_2.OH$.

(1299) METHYLBENZENE OR TOLUENE: C_7H_8 or $C_6H_5.CH_3.=92$.—Toluene is produced by the action of sodium on a mixture of bromobenzene and iodomethane or methylic iodide: $C_6H_5Br + CH_3I + 2Na = C_6H_5.CH_3 + NaI + NaBr$; by distilling the isomeric methylbenzoic or toluic acids with an excess of calcic hydrate: $C_6H_4(CH_3).COOH + Ca(OH)_2 = C_6H_5.CH_3 + CaCO_3 + OH_2$; and by heating benzylic alcohol with a concentrated alcoholic solution of potassic hydrate, and then distilling: when the whole of the alcohol has passed over, and the residue has become solid, the toluene distils over mixed with undecomposed benzylic alcohol (Cannizzaro):

$$\underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2(OH)} + KHO = \underset{\text{Potassic benzoate.}}{C_6H_5.COOK} + \underset{\text{Toluene.}}{C_6H_5.CH_3} + 2OH_2.$$

Toluene is a product of the dry distillation of tolu-balsam and many other resins, but it is almost always prepared by the fractional distillation of that portion of coal oil which boils at about 100°—120° (212°—248° F.).

Toluene is a colourless liquid closely resembling benzene in its physical properties, but does not solidify even when cooled to —20° (—4° F.); it boils at 111°(231°·8 F.), and at 0° (32° F.) has the sp. gr. 0·882. When oxidized with chromic or dilute nitric acid, it furnishes benzoic acid; and if heated to 260° (500° F.) with iodine, benzyltoluene, $C_6H_5.CH_2.C_6H_4.CH_3$, together with benzene and the hydrocarbon $C_{28}H_{22}$ are formed (Schützenberger, *Deut. chem. Ges. Ber.*, v. 1109).

(1300) HYDROCARBONS: $C_8H_{10}=106$.—Four hydrocarbons of this composition are known, viz., *Ethylbenzene,* and three isomeric *dimethylbenzenes* or *xylenes.*

Ethylbenzene or *Ethylphenyl,* $C_6H_5.C_2H_5$, is obtained by the action of sodium on a mixture of bromobenzene and bromethane or ethylic bromide diluted with ether. The following directions for its preparation are given by Fittig and König (*Ann. Chem. Pharm.*, cxliv. 277).

Ordinary ether is allowed to remain in contact with a considerable amount of calcic chloride for twenty-four hours; a quantity about double the volume of the mixed bromides is then introduced into a flask, and sodium is added cut in very thin slices, about 1½ times as much as is theoretically required for the decomposition of the bromides (p. 276). The flask is connected with a reversed condenser, and is placed in a large vessel filled with cold water. At first a violent evolution of hydrogen is observed, but after a few hours this entirely ceases, the temperature of the water is then reduced to 0° (32° F.) by means of ice, and the carefully dried mixture of bromides is added. A slight excess (about one-fourth more than the theoretical amount) of the ethylic bromide should be taken. As a rule the action soon sets in, which may be known by the pieces of sodium becoming blackened and sinking to the bottom, but sometimes the sodium remains bright for a day or more. When the action has once commenced, however, it is soon completed, usually in one to two hours; during this time great care must be taken that the temperature of the water does not rise, for so much heat is evolved that notwithstanding the cooling, the ether boils, and in part distils over. The more quietly and slowly the action takes place, the greater is the yield, so that it is also desirable on this account not to operate with larger quantities than 100 grams of bromobenzene. When the reaction is completed, the ether is distilled off on the water-bath; the flask is then suspended by the neck, and the product is rapidly distilled off over a bare flame. Care must be taken not to heat the bottom of the flask too strongly at first; and, in fact, the operation succeeds best when the heat is applied by waving a large gas flame round and round the flask, so that only its sides are heated. In this way it is possible to avoid the breaking of the flask, which usually occurs when a sand-bath or wire gauze is used. The distillate consists almost entirely of ethylbenzene, and is purified by fractional distillation. A similar course is to be recommended in the preparation of other homologues of benzene.

Ethylbenzene is a colourless mobile liquid resembling toluene; it boils at 134° (273°·2 F)., and at 22°·5 (72°·5 F.) has the sp. gr.

0·8664. When oxidized with potassic dichromate and sulphuric acid mixture, or with dilute nitric acid (1 vol. of nitric acid of sp. gr. 1·4 and 2 vols. water), it yields benzoic acid:

$$\underset{\text{Ethylbenzene.}}{C_6H_5.C_2H_5} + 3O_2 = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + CO_2 + 2OH_2.$$

Paradimethylbenzene or *Paraxylene*: $C_6H_4(CH_3)_2$, ($CH_3 : CH_3 = 1 : 4$).—This hydrocarbon is obtained by the action of sodium on a mixture of crystalline parabromotoluene and methylic iodide, diluted with pure benzene (Jannasch, *Ann. Chem. Pharm.*, clxxi. 79), or on a mixture of crystalline paradibromobenzene and methylic iodide, diluted with ether (V. Meyer, *ibid.* clvi. 282). It crystallizes when pure in large monoclinic prisms, which melt at 15° (59° F.); it boils at 136°—137° (276°·8—278°·6 F.) (Jannasch). Paradimethylbenzene is readily oxidized by dilute nitric acid to paramethylbenzoic or paratoluic acid, $C_6H_4(CH_3).COOH$, and by chromic acid to terephthalic acid, $C_6H_4(COOH)_2$.

Metadimethylbenzene or *Metaxylene*: $C_6H_4(CH_3)_2$, ($CH_3 : CH_3 = 1 : 3$).—Xylene or xylol, from coal tar (the portion boiling at 136°—140° (276°·8—284° F.), contains para- and metaxylene in variable proportions, but usually consists mainly of metaxylene; other hydrocarbons, however, are present, the nature of which is unknown (Fittig, *ibid.* cliii. 273). Pure metaxylene is obtained by distilling xylic or mesitylenic acids, $C_6H_3(CH_3)_2.COOH$, with calcic hydrate (Fittig and Bieber, *ibid.* clvi. 235; Fittig and Velguth, cxlviii. 1). It boils at 137°—137°·5 (278°·6—279°·5 F.). Metaxylene is *not* oxidized by dilute nitric acid, but is slowly converted by oxidation with chromic acid into isophthalic acid, $C_6H_4(COOH)_2$.

Xylene from coal tar has a peculiar faint odour different from that of benzene; its specific gravity at 19° (66°·2 F.) is 0·86.

Orthodimethylbenzene or *Orthoxylene*: $C_6H_4(CH_3)_2$, ($CH_3 : CH_3 = 1 : 2$), is obtained by the action of sodium on a mixture of orthobromotoluene and methylic iodide; and by distilling paraxylic acid, $C_6H_3(CH_3)_2.COOH$, with calcic hydrate. It is a colourless limpid liquid like its isomerides, but has a much less pleasant odour, and boils at 140°—141° (284°—285°·8 F.). Dilute nitric acid oxidizes it to orthomethylbenzoic or orthotoluic acid, but it is entirely decomposed when oxidized with chromic acid (Fittig and Bieber, *ibid.* clvi. 239).

The three isomeric dimethylbenzenes are characterized and distinguished not only by their oxidation products, but also by their behaviour with nitric acid: when treated with a mixture of concentrated nitric and sulphuric acids, para- and metadimethylbenzene are readily converted into *crystalline trinitro*-derivatives, the change taking place even at the ordinary temperature, if allowed to stand some time; orthodimethylbenzene, however, is only converted with extreme difficulty into crystalline nitro-derivatives, it being necessary to warm it for 8 to 10 hours with the acid mixture in order to obtain them. Trinitropara- and metaxylene are readily distinguished, since the latter is much less soluble in alcohol than the former, and melts at 177° (350°·6 F.), trinitroparadimethylbenzene melting at 137° (278°·6 F.).

(1301) HYDROCARBONS, $C_9H_{12}=120$.—Several of these have been obtained—viz., *Propylbenzene, Isopropylbenzene, Ethylmethylbenzene,* and two *Trimethylbenzenes.*

Propylbenzene : $C_6H_5.CH_2.CH_2.CH_3$, is obtained by the action of sodium on a mixture of bromobenzene and propylic bromide. It is a colourless, pleasant smelling liquid, which boils at 157° (314°·6 F.); when oxidized it yields benzoic acid.

Isopropylbenzene or *Cumene :* $C_6H_5.CH(CH_3)_2$.—When cumic acid, $C_6H_4(C_3H_7).COOH$, is distilled with calcic hydrate, a hydrocarbon of the composition C_9H_{12} is obtained, boiling at 151° (303°·8 F.), which, like the synthetically prepared propylbenzene, is converted into benzoic acid by oxidation: it is, therefore, concluded that cumene from cumic acid is an isopropylbenzene. The attempts, however, to prepare it by Fittig's method from bromobenzene and isopropylic iodide have failed until recently; Jacobsen (*Deut. chem. Ges. Ber.*, viii. 1260) finds, however, that if slices of sodium are introduced into isopropylic iodide, which is then covered with a layer of a solution of bromobenzene in six times its volume of pure ether, and the mixture left at rest, action gradually takes place. If the mixture is then boiled for a few hours, and afterwards distilled, the unattacked iodide passes over, together with much diphenyl, and a very small quantity of a fraction boiling at 145°—155° (293°—311° F.). When this is fractionally distilled, and the portion boiling at about 150° (302° F.) is treated with sulphuric acid, a sulpho-acid is formed yielding salts which differ from those of propylbenzenesulphonic acid, but are precisely similar to those furnished by the sulpho-acid of cumene from cumic acid.

Ethylmethylbenzene : $CH_3.C_6H_4.C_2H_5$.—By the action of sodium on a mixture of bromotoluene and ethylic bromide, Glinzer and Fittig (*Ann. Chem. Pharm.*, cxxxvi. 312) obtained an ethylmethylbenzene boiling at 159° (318°·2 F.), of the sp. gr. 0·8652 at 21°

(69°·8 F.), which gave terephthalic acid on oxidation. The bromotoluene employed was that directly produced by the action of bromine on cooled toluene, but as it has since been shown that this is a mixture of parabromotoluene with more or less orthobromotoluene, there can be little doubt that the hydrocarbon obtained was a mixture of para- and orthethylmethylbenzene. Pure parethylmethylbenzene has been prepared by Jannasch and Dieckmann (*Deut. chem. Ges. Ber.*, vii. 1513) by the action of sodium on a mixture of crystalline parabromotoluene and ethylic iodide, diluted with benzene. It boils at 161°—162° (321°·8—323°·6 F.), and does not solidify at −20° (−4° F.); when oxidized with dilute nitric acid, it gave pure paratoluic acid.

According to Wroblevsky (*ibid.* viii. 573), metabromotoluene is converted into metethylmethylbenzene by the action of ethylic bromide and sodium. This hydrocarbon furnishes isophthalic acid on oxidation.

Mesitylene (*Trimethylbenzene*): $C_6H_3(CH_3)_3$. ($CH_3 : CH_3 : CH_3 = 1 : 3 : 5$).—This hydrocarbon has not been obtained from benzene by synthesis, but is always prepared by distilling acetone with sulphuric acid.

The following is the method of proceeding recommended by Fittig and Brückner (*Ann. Chem. Pharm.*, cxlvii. 42).

A quantity of dry sand is placed in a large tubulated retort, and 1 vol. of commercial acetone is added; a cooled mixture of 1 vol. concentrated sulphuric acid and ½ vol. water is then introduced in a slow continuous stream, and the mixture allowed to stand during at least 24 hours. The retort is then connected with a condenser, and the distillation commenced; at first acetone and water pass over. When oily streaks are observed in the upper part of the retort the receiver is changed; a yellow coloured oil then distils, consisting chiefly of mesitylene. The distillation is continued as long as oil passes over. At a certain period of the process, an evolution of sulphurous acid sets in, and the contents of the retort become of a deep indigo-blue colour, which only disappears towards the close of the operation. The crude oil is washed with sodic hydrate solution, and with water; dried with calcic chloride, and fractionally distilled from metallic sodium. Although the yield is small in proportion to the amount of acetone employed, it is possible by working with 3 or 4 retorts at a time to prepare without difficulty a pound of pure mesitylene in a week.

When allylene gas (1252) is passed into concentrated sulphuric acid, it is absorbed, and on adding a *small quantity* of water, and distilling, mesitylene is obtained (Fittig and Schrohe, *ibid.* viii. 17 and 367).

The portion of coal-tar oil which boils at 164°—167° 327°·2—332°·6 F.) consists chiefly of mesitylene. Mesitylene is also present amongst the hydrocarbons obtained by the action of zincic chloride on camphor (Fittig and Wackenroder, *ibid.* cli. 292).

Mesitylene is a colourless, mobile, highly refractive liquid of peculiar, not unpleasant odour; it boils at 163° (325°·4 F.). When oxidized with a mixture of potassic dichromate and sulphuric acid, it yields acetic acid only, and is thus distinguished from all the other known hydrocarbons of the benzene series. If treated with dilute nitric acid, however, it is converted into a mixture of mesitylenic acid, $C_6H_3(CH_3)_2(COOH)$, and mesidic or uvitic acid, $C_6H_3(CH_3)(COOH)_2$; and these acids when oxidized with chromic acid readily furnish trimesic acid, $C_6H_3(COOH)_3$. When it is heated with phosphonic iodide, PH_4I, to 280° (536° F.), it is converted into a hydrocarbon of the C_nH_{2n} series, C_9H_{18}, which boils at 138° (280°·4 F.) (Baeyer).

Pseudocumene (*Trimethylbenzene*): $C_6H_3(CH_3)_3$, $(CH_3:CH_3:CH_3 = 1:3:4)$.—Pseudocumene has been prepared by the action of sodium and methylic iodide on the monobromo-derivatives of the three isomeric dimethylbenzenes, and on the dibromotoluene prepared by the action of bromine on toluene in presence of iodine (Fittig and Laubinger, *ibid.* cli. 257; Fittig and Jannasch, *ibid.* cli. 283; Jannasch, *ibid.* clxxvi. 283). It is also a constituent of the portion of coal-tar oil boiling at 164°—167° (327°·2—332°·6 F.).

Pure pseudocumene from crystalline bromoparaxylene boils at 166°—167° (330°·8—332°·6 F.), and does not solidify at −20° (−4° F.) (Jannasch). When oxidized with dilute nitric acid, pseudocumene furnishes a mixture of the two isomeric monobasic acids, *xylic* acid and *paraxylic* acid, $C_6H_3(CH_3)_2(COOH)$, with the dibasic *xylidic acid*, $C_6H_3(CH_3)(COOH)_2$. By the action of a mixture of concentrated nitric and sulphuric acids, pseudocumene is converted into a crystalline trinitro-derivative, $C_6(CH_3)_3(NO_2)_3$, which melts at 185° (329° F.), and is thus distinguished from mesitylene, which when similarly treated yields trinitromesitylene, melting at 232° (449°·6 F.); moreover, trinitropseudocumene is readily reduced by ammonic sulphide and converted into nitroamidopseudocumene, $C_6H(CH_3)_3(NO_2)(NH_2)$, whilst trinitromesitylene is converted into dinitroamidomesitylene, $C_6(CH_3)_3(NO_2)_2(NH_2)$, by the same reagent.

(1302) HYDROCARBONS: $C_{10}H_{14} = 134$.—No less than seven of these are known, viz.: *β-Butylbenzene*, *Parapropylmethylbenzene* or *Cymene*, *Paradiethylbenzene*, two isomeric *Ethyldimethylbenzenes*, and two isomeric *Tetramethylbenzenes*.

β-Butylbenzene: $C_6H_5.CH_2.CH(CH_3)_2$. — This hydrocarbon is obtained although only in small quantity, by the action of sodium on a mixture of bromobenzene and isoprimary butylic bromide, and more easily by its action on a mixture of benzylic chloride and isopropylic iodide. It boils at 159°—161° (318°·2—321°·8 F.); it is converted into benzoic acid by oxidation (Riess, *Deut. chem. Ges. Ber.*, iii. 779).

Parapropylmethylbenzene or *Cymene* : $C_6H_4\begin{cases}CH_3\\C_3H_7\end{cases}$, ($CH_3 : C_3H_7 = 1 : 4$).—Cymene exists together with terpenes in a number of the so-called essential-oils* (1278), such as oil of cumin, the oil of the *Ptychotis Ajowan,* the oil of the water hemlock (*Cicuta virosa*), the oil of the *Eucalyptus globulus,* oil of nutmeg, &c. It may be obtained by the action of sodium on a mixture of crystalline parabromotoluene and normal propylic bromide (Fittica, *Ann. Chem. Pharm.*, clxxii. 320); and it is thus proved that cymene contains *normal propyl,* and that it is a member of the *para-* series of di-derivatives of benzene: the latter conclusion may also be inferred from the conversion of cymene into terephthalic acid by oxidation. Cymene may be prepared by the action of phosphoric anhydride, pentasulphide, or pentachloride, or of zincic chloride, on camphor and several other oxygenated bodies of the composition $C_{10}H_{14}O$, present in various essential oils (viz.: myristicol from oil of nutmeg, and absinthol from oil of wormwood); in these cases the action amounts simply to the withdrawal of the elements of a molecule of water from the oxygenated body, but when phosphoric pentasulphide is employed hydric sulphide is evolved:

$$\underset{\text{Camphor.}}{6C_{10}H_{16}O} + P_2S_5 = \underset{\text{Cymene.}}{6C_{10}H_{14}} + 5SH_2 + 2HPO_3;$$

and by the action of phosphoric pentachloride a chlorinated compound is first produced, which is subsequently resolved by distillation into cymene and hydrochloric acid:

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} + PCl_5 = C_{10}H_{16}Cl_2 + POCl_3;$$

$$C_{10}H_{16}Cl_2 = C_{10}H_{14} + 2HCl.$$

$$\underset{\text{Myristicol.}}{C_{10}H_{15}.OH} + PCl_5 = C_{10}H_{15}Cl + POCl_3 + HCl;$$

$$C_{10}H_{15}Cl = C_{10}H_{14} + HCl.$$

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* Wright is of the opinion that the small quantity of cymene met with in some essential oils is perhaps formed by the oxidation of a portion of the terpene, and the subsequent resolution of the oxidized body ($C_{10}H_{16}O$) into cymene and water during distillation.

Cymene is also obtained on distilling thymol and carvacrol, $C_{10}H_{14}O$, with ter- or pentasulphide of phosphorus.

Cymene may readily be prepared by the action of phosphoric anhydride or pentasulphide on camphor. If the former be employed, it is mixed with the camphor in the proportions indicated by the equation:

$$C_{10}H_{16}O + P_2O_5 = C_{10}H_{14} + 2HPO_3,$$

and gently heated in a flask, attached to a condenser, until the reaction commences, which is evidenced by the mixture at the bottom of the flask becoming brown: the reaction then extends to the whole mass somewhat rapidly. The liquid product is afterwards poured off from the cake of metaphosphoric acid at the bottom of the flask, and digested with a small quantity of phosphoric anhydride. This treatment is then repeated, and finally the product is fractionally distilled from sodium. In this manner 60 to 80 per cent. of cymene may be obtained (Fittica, *ibid.* 307).

Somewhat less cymene is produced by the action of phosphoric pentasulphide, but, on the other hand, the latter is far more readily prepared than phosphoric anhydride. The camphor and phosphoric pentasulphide mixed in the proportions of about 3 to 1 are placed in a flask attached to a condenser, and a gentle heat applied; the reaction soon takes place, and much hydric sulphide is evolved. In order to decompose all the camphor the mixture is gently boiled for a couple of hours and then distilled; the distillate is violently agitated with a concentrated solution of sodic hydrate to remove the thiocymene, $C_{10}H_{13}.SH$, present, then with water, and afterwards several times with small quantities of concentrated sulphuric acid; it is finally washed with water, dried over calcic chloride, and distilled from sodium.

Pure cymene is a colourless, mobile, highly refractive liquid of peculiar, not unpleasant, odour; it boils at 175° (347° F.), and at 0° (32° F.) has the sp. gr. 0·870. When oxidized with dilute nitric acid it furnishes *paratoluic acid,* $C_6H_4(CH_3).COOH$, together with terephthalic acid, $C_6H_4(COOH)_2$, and a considerable quantity of acetic acid (Kekulé and Dittmar, *Deut. chem. Ges. Ber.*, iii. 894); chromic acid also oxidizes it to terephthalic acid.

Constitution of the terpenes.—All the terpenes appear to be capable of yielding cymene when two atoms of hydrogen are withdrawn from them. This may be effected, however, in various ways. The most advantageous method is probably that employed by Kekulé and Oppenheim (*ibid.* vi. 437 and 915; vii. 625), which consists in gradually adding iodine to the terpene, digesting the mixture for some hours in a flask attached to a reversed condenser, and distilling; the distillate is then washed with an alkaline solution and the cymene purified by fractional distillation from sodium. The first action appears to consist in the combination of a molecule of the terpene with a molecule of iodine, the resulting compound, when heated, being resolved into cymene and hydriodic acid.

By very carefully adding a molecule of bromine to a molecule of a terpene which is well cooled, a compound of the two is obtained, which, on treatment in various ways, furnishes cymene. In some cases it is merely necessary to distil several times: thus, although the bromide of ordinary turpentine oil furnishes very little cymene when treated in this manner, yet, as Wright has shown (*Journ. Chem. Soc.*, xxvi. 691), hesperidene, the terpene from nutmeg-oil, yields a very large proportion of cymene when its bromide is several times distilled. Oppenheim finds (*Deut. chem. Ges. Ber.*, v. 94 and 628) that a considerable amount of cymene may be obtained from the bromide of turpentine oil by heating it with a slight excess of aniline for eight hours to about 190° (374° F.) in sealed tubes:

$$\underset{\text{Turpentine bromide.}}{C_{10}H_{16}Br_2} + \underset{\text{Aniline.}}{2C_6H_7N} = \underset{\text{Cymene.}}{C_{10}H_{14}} + \underset{\text{Aniline hydrobromide.}}{2C_6H_8NBr.}$$

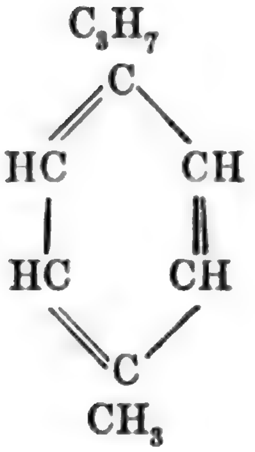
To purify the product, the mixture from the tubes is rendered acid with dilute sulphuric acid, and the hydrocarbon distilled over in a current of steam; it is then dried and distilled from sodium.

Wright has also shown (*Journ. Chem. Soc.*, xxvii. 620) that cymene is formed in small quantity from terpenes by the action of phosphoric pentasulphide, and according to Riban, a little cymene may be produced from terpenes by treating them with sulphuric acid and distilling:

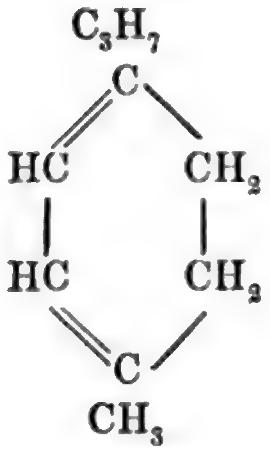
$$C_{10}H_{16} + H_2SO_4 = C_{10}H_{14} + SO_2 + 2OH_2.$$

By these various methods cymene has been obtained from ordinary turpentine oil, and from terebene; from the terpenes of nutmeg oil, orange-peel oil, lemon oil, and eucalyptus oil; and from the terpenes obtained by the action of phosphoric anhydride or pentasulphide on borneol, geraniol, citronellol, and cajeputol, all of which have the formula $C_{10}H_{18}O$.

The fact that the various terpenes are thus convertible into cymene, together with the circumstance that they combine with *at most* four atoms of monad elements (in the formation of the dihydrochlorides), has led chemists to regard them as *dihydrides of cymene*; thus:

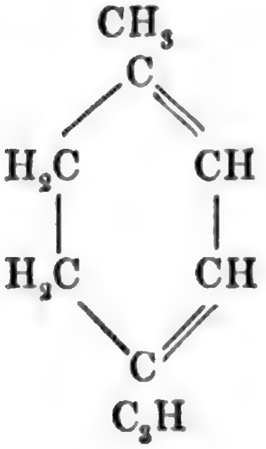


Cymene.

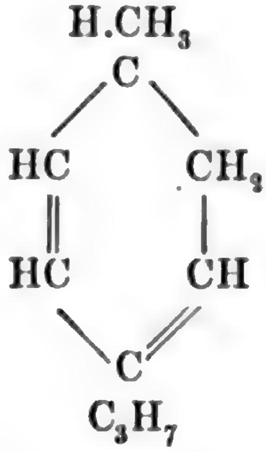


Cymene dihydride.

But cymene is a *para*propylmethylbenzene, and according to Kekulé's hypothesis it can only give rise to *three isomeric* dihydrides, viz.:



I.



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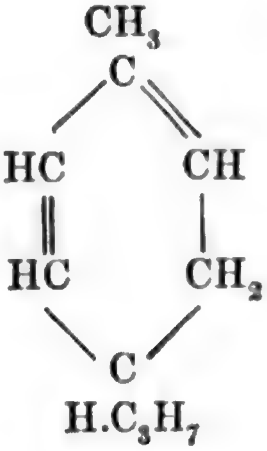


III.

Since more than three isomeric terpenes undoubtedly exist, the conclusion is therefore forced upon us, that all these, although they furnish cymene, are not hydrides of a *para*propylmethylbenzene, but that some of them are hydrides of isomeric propylmethylbenzenes, and some perhaps hydrides of isopropylmethylbenzenes, and that isomeric change takes place during their conversion into cymene.

With regard to the existence of a considerable number of isomeric terpenes, it is to be borne in mind that we are totally unaware of the nature of the isomerism which obtains, for example, between the terpenes present in the so-called French and English turpentine oils: in their chemical behaviour they exhibit the most perfect resemblance, and yet they are so very different optically. The only assumption we can make which is any way applicable to the explanation of this remarkable difference, is that the molecules of the terpenes in the liquid state are complex molecules formed by the coalescence of a number of simple molecules, and that the physical difference between the two terpenes in question results from a different arrangement of the simple molecules which we may suppose are identical. If this be the case, a comparatively limited number of chemically identical terpenes may exist, and yet, as seems to be the case according to our present knowledge, the number which exhibit physical differences may be very large.

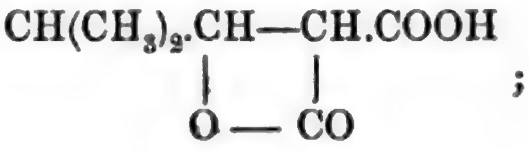
Apart from the formation of cymene from the terpenes, there is no evidence proving that the C_3H_7 group, which, it is supposed, is present in all the terpenes, is *propyl* and not *isopropyl*. The behaviour of the oxidation products of ordinary turpentine oil appears rather to favour the conclusion that it is isopropyl. Thus when turpentine oil is oxidized with dilute nitric acid, the so-called *diaterebic acid*, $C_7H_{12}O_5$, is produced, but this very readily loses a molecule of water and is converted into *terebic* acid, $C_7H_{10}O_4$; on distilling terebic acid, *pyroterebic acid*, $C_6H_{10}O_2$, is obtained, and this, when heated with hydriodic acid, is converted into a *caproic acid*, $C_6H_{12}O_2$, identical with that formed from isoprimary (fermentation) amylic alcohol. This caproic acid is represented by the formula:

$$CH(CH_3)_2.CH_2.CH_2.COOH,$$

and there can be little doubt, therefore, that all the acids mentioned contain isopropyl, their most probable formulæ being

$$CH(CH_3)_2.CH(OH).CH(COOH)_2;$$

Diaterebic acid.



$$CH(CH_3)_2.\underset{\underset{\displaystyle O\text{—}CO}{|\quad\quad|}}{CH\text{—}CH}.COOH \quad ;$$

Terebic acid.

$$CH(CH_3)_2.CH{=}CH.COOH.$$

Pyroterebic acid.

Hence it would seem probable also that turpentine is an isopropyl derivative (Fittig and Mielck, *Deut. chem. Ges. Ber.*, vii. 649). From these considerations it is evident that we must regard the constitution of the terpenes and the nature of their relation to cymene as problems still far from being solved.

Paradiethylbenzene: $C_6H_4(C_2H_5)_2$, $(C_2H_5 : C_2H_5 = 1 : 4)$.—Fittig and König (*Ann. Chem. Pharm.*, cxliv. 285) obtained this hydrocarbon by the action of sodium on a mixture of bromethylbenzene and ethylic bromide. Since the action of bromine on methylbenzene or toluene leads to the formation of two isomeric bromotoluenes, it is highly probably that this is also the case with ethylbenzene, and that therefore Fittig and König's product was a mixture of *para*- and *ortho*diethylbenzene. Diethylbenzene is a colourless liquid of pleasant odour, which boils at 178°—179° (352°·4—354°·2 F.) of the sp. gr. 0·870 at 15°·5 (59°·9 F.). When oxidized with dilute nitric acid it furnishes ethylbenzoic acid, $C_6H_4(C_2H_5).COOH$, but chromic acid oxidizes it to terephthalic acid.

Ethyldimethylbenzene: $C_6H_3(CH_3)_2(C_2H_5)$, $(CH_3 : CH_3 : C_2H_5 = 1 : 3 : 4)$.—By acting on bromoxylene with ethylic bromide and sodium, Fittig and Ernst (*ibid.* cxxxix. 192) obtained an ethyldimethylbenzene in all probability consisting chiefly of the modification $(CH_3 : CH_3 : C_2H_5 = 1 : 3 : 4)$, but also containing the modification $(CH_3 : C_2H_5 : CH_3 = 1 : 2 : 4)$, as coal tar xylene was employed. The hydrocarbon thus prepared boils at 183°—184° (361°·4—363°·2 F.), and at 20° (68° F.) has the sp. gr. 0·8783.

Ethyldimethylbenzene: $C_6H_3(CH_3)_2(C_2H_5)$, $(CH_3 : CH_3 : C_2H_5 = 1 : 3 : 5)$.—This hydrocarbon may be said to be the true homologue of mesitylene, and to be the second term of the series of hydrocarbons formed from benzene by the displacement of three atoms of hydrogen by radicles of the form C_nH_{2n+1}, these radicles being moreover symmetrically placed. It is produced by a method similar to that which furnishes mesitylene, viz., by distilling a mixture of dimethylketone or acetone and methylethylketone with sulphuric acid (Jacobsen, *Deut. chem. Ges. Ber.*, vii. 1430):

$$\underset{\text{Dimethylketone.}}{2CH_3.CO.CH_3} + \underset{\text{Ethylmethylketone.}}{C_2H_5.CO.CH_3} - 3OH_2 = \underset{\text{Ethyldimethylbenzene.}}{C_6H_3(C_2H_5)(CH_3)_2}.$$

It boils at 180°—182° (356°—359°·6 F.), and at 20° (68° F.) has the sp. gr. 0·864. When oxidized by dilute nitric acid it furnishes mesitylenic acid, $C_6H_3(CH_3)_2.COOH$.

Tetramethylbenzene: $C_6H_2(CH_3)_4$, $(CH_3 : CH_3 : CH_3 : CH_3 = 1 : 2 : 3 : 5)$.—When a mixture of methylic iodide and bromomesitylene dissolved in pure benzene is heated with sodium to about 150° (302° F.) a reaction takes place, and by submitting the product to fractional distillation a hydrocarbon of the composition $C_{10}H_{14}$ may be isolated. It boils at 192°—194° (377°·6—381°·2 F.), and does not solidify when cooled in a mixture of ice and salt (Jannasch, *ibid.* viii. 355).

Tetramethylbenzene or *Durene:* $C_6H_2(CH_3)_4$.—A mixture of methylic iodide with monobromopseudocumene dissolved in ether, is slowly acted on by sodium at the ordinary temperature, a crystalline tetramethylbenzene being produced. Durene, as this hydrocarbon has been termed, crystallizes from alcohol in prisms;* it melts at 80° (176° F.), and boils at 189°—191° (372°·2—375°·8 F.) (Fittig and Jannasch, *Zeits. chem.* [2], vi. 161). When oxidized

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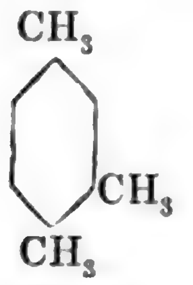
* Paradimethylbenzene or paraxylene and durene (tetramethylbenzene) are the only two crystalline hydrocarbons which have been obtained from benzene, which itself crystallizes; it is noteworthy that, starting with benzene and passing from it through toluene to paraxylene, and thence through pseudocumene to durene, the intermediate terms of this series are liquid, and there is a peculiar relation in the boiling-points, the difference between each solid and the next higher liquid hydrocarbon being 30° (Cent.) and between the liquid and the next higher solid hydrocarbon 25°; thus:

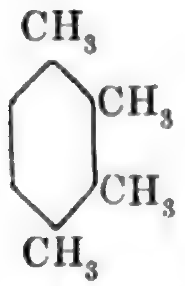
	Benzene.	Toluene.	Paraxylene.	Pseudocumene.	Durene.
Melting point	7°	liquid.	15°	liquid.	80°.
Boiling point	81°	111°	136°·5	166°	191°.

with dilute nitric acid, it furnishes a mixture of *cumylic* acid, $C_6H_2(CH_3)_3.COOH$, and *cumidic* acid, $C_6H_2(CH_3)_2(COOH)_2$ (Jannasch, *ibid.* vi. 449; vii. 33). Durene may also be obtained by the action of sodium on a mixture of methylic iodide and the dibromoxylene from coal tar xylene (Jannasch, *Deut. chem. Ges. Ber.*, vii. 692).

Since mesitylene has the constitution ($CH_3 : CH_3 : CH_3 = 1 : 3 : 5$) it is only possible to obtain from it a single tetramethylbenzene, but pseudocumene may furnish three modifications of tetramethylbenzene; thus:



Pseudocumene.



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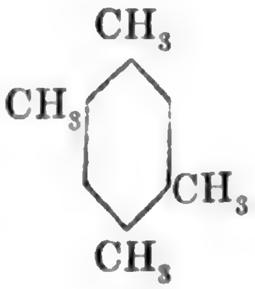

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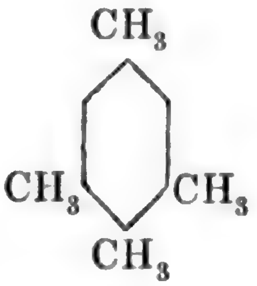

III.

One of these (III.) it will be seen, is identical with that derived from mesitylene, and the constitution of durene must therefore be that expressed by fig. I or fig. II. At present there is not sufficient experimental evidence to decide which of these should be adopted, but the latter appears to be the more probable.

(1303) HYDROCARBONS: $C_{11}H_{16} = 148$.—Five of these are known, viz.: two isomeric *Amylbenzenes*, two isomeric *Propyldimethylbenzenes*, and a *Diethylmethylbenzene*.

β-Amylbenzene: $C_6H_5.CH_2.CH_2.CH(CH_3)_2$, is formed by the action of sodium on a mixture of bromobenzene and isoprimary amylic bromide.[*] It is a liquid of peculiar odour, quite different from that of benzene; it boils at 193° (379°·4 F.). When oxidized, it furnishes benzoic acid.

θ-Amylbenzene: $C_6H_5.CH(C_2H_5)_2$.—Lippmann and Louguinine (*ibid.* cxlv. 106) obtained this hydrocarbon by the action of zincic ethide dissolved in benzene, on a benzene solution of the compound $C_6H_5.CHCl_2$ from toluene:

$$C_6H_5.CHCl_2 + 2Zn(C_2H_5)_2 = C_6H_5.CH(C_2H_5)_2 + ZnClC_2H_5.$$

After purification by heating with sodium in sealed tubes to 200° (392° F.), it boils at about 178° (352°·4 F.); its sp. gr. at 0° (32° F.) being 0·875.

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[*] Isoprimary amylic bromide is obtained from fermentation amylic alcohol, which appears, however, to be a mixture of the *two* isoprimary amylic alcohols $CH(CH_3)_2.CH_2.CH_2(OH)$ and $CH\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}.CH_2(OH)$, the former being the chief constituent (see amylic alcohols): hence all the amyl derivatives of benzene obtained with it are doubtless mixtures of β-amyl—$CH(CH_3)_2.CH_2.CH_2$—and γ-amyl—$CH\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}.CH_2$—compounds.

Propyldimethylbenzene: $C_6H_3(C_3H_7)(CH_3)_2$, ($CH_3 : CH_3 : C_3H_7 = 1 : 3 : 5$).—This hydrocarbon is the third term of the "mesitylene series," and is obtained by distilling a mixture of dimethylketone and propylmethylketone with sulphuric acid (Jacobsen, *Deut. chem. Ges. Ber.*, viii. 1258). It boils at 206°—210° (402°·8—410° F.). When oxidized with dilute nitric acid it furnishes mesitylenic acid.

Laurene: $C_6H_3(C_3H_7)(CH_3)_2$.—Laurene is obtained, together with other products, when camphor is distilled with zincic chloride (Fittig, Köbrich and Jilke, *Ann. Chem. Pharm.*, cxlv. 149). It boils at about 188° (370°·4 F.), and at 10° (50° F.) has the sp. gr. 0·887. It is oxidized by dilute nitric acid to an acid of the composition $C_6H_3(CH_3)_2.COOH$, which appears to be identical with the paraxylic acid from pseudocumene. It is not known whether laurene is a propyl or isopropyl derivative, but from the lowness of its boiling-point as compared with that of the propyldimethylbenzene above described, it appears not unlikely that it is an isopropyldimethylbenzene.

Diethylmethylbenzene: $C_6H_3(C_2H_5)_2(CH_3)$, ($CH_3 : C_2H_5 : C_2H_5 = 1 : 3 : 5$).—This hydrocarbon, which is also a member of the mesitylene series, is formed on distilling a mixture of dimethylketone and ethylmethylketone with sulphuric acid (Jacobsen). It boils at 198°—200° (388°·4—392° F.), and at 20° (68° F.) has the sp. gr. 0·879. By long boiling with dilute nitric acid it is oxidized to uvitic acid, $C_6H_3(CH_3)(COOH)_2$.

Hydrocarbons: $C_{12}H_{18} = 162$.—Only three such are known, viz.: *β-Hexylbenzene*, *β-Amylmethylbenzene* and *Triethylbenzene*.

(1304) *β-Hexylbenzene:* $C_6H_5.CH_2.CH_2.CH_2CH(CH_3)_2$, is obtained by the action of sodium on a mixture of benzylic chloride, $C_6H_5.CH_2Cl$, and isoprimary amylic bromide (Aronheim, *Ann. Chem. Pharm.*, clxxi. 223). It boils at 214°—215° (417°·2—419° F.).

β-Amylmethylbenzene: $C_6H_4\left\{\begin{array}{l}CH_3\\CH_2.CH_2.CH(CH_3)_2.\end{array}\right.$—Fittig and Bigot (*ibid.* cxli. 162) prepared this hydrocarbon from bromotoluene and isoprimary amylic bromide by the action of sodium. As they employed crude bromotoluene, their product was doubtless a mixture of *para-* and *ortho-* β-amylmethylbenzene. It boiled at 213° (415°·4 F.), and at 9° (48°·2 F.) had the sp. gr. 0·864. When oxidized with chromic acid, it gave terephthalic and acetic acids.

Triethylbenzene: $C_6H_3(C_2H_5)_3$, ($C_2H_5 : C_2H_5 : C_2H_5 = 1 : 3 : 5$).—The only known triethylbenzene belongs to the mesitylene series, being obtained by distilling ethylmethylketone with sulphuric acid (Jacobsen):

$$\underset{\text{Ethylmethylketone.}}{3C_2H_5.CO.CH_3} - 3OH_2 = \underset{\text{Triethylbenzene.}}{C_6H_3(C_2H_5)_3}.$$

It boils at 217°—220° (422°·6—428° F.); when oxidized with chromic acid it appears to furnish trimesic acid, $C_6H_3(COOH)_3$.

(1305) HYDROCARBONS: $C_{13}H_{20} = 176$.—Two only are known, viz.: *β-Amyldimethylbenzene* and *Methyldipropylbenzene*.

β-Amyldimethylbenzene: $C_6H_3\left\{\begin{array}{l}(CH_3)_2\\CH_2.CH_2\,CH(CH_3)_2.\end{array}\right.$—Fittig and Bigot obtained this hydrocarbon by the action of sodium on a mixture of isoprimary amylic bromide and bromoxylene. As coal-tar xylene was employed, their product was doubtless a mixture of the modifications ($CH_3 : CH_3 : C_5H_{11} = 1 : 3 : 4$) and ($CH_3 : C_5H_{11} : CH_3 = 1 : 3 : 4$). It boiled at 232°—233° (449°·6—451°·4 F.), and at 9° (48°·2 F.) had the sp. gr. 0·895.

Methyldipropylbenzene: $C_6H_3(CH_3)(C_3H_7)_2$, ($CH_3 : C_3H_7 : C_3H_7 = 1 : 3 : 5$).—This homologue of mesitylene is formed by distilling a mixture of dimethylketone and propylmethylketone with sulphuric acid (Jacobsen). It boils at 243°—248° (469°·4—478°·4 F.); when oxidized with dilute nitric acid it furnishes uvitic acid, $C_6H_3(CH_3)(COOH)_2$.

(1306) HYDROCARBONS: $C_{15}H_{24} = 204$.—It has already been mentioned that a number of these hydrocarbons are contained in various "essential oils." At present nothing whatever is known of their nature, but from their occurrence in plants together with propyl-derivatives the assumption that they are *tripropyl-derivatives of benzene* does not appear improbable. A short account of some of the oils which contain these hydrocarbons may conveniently be given here.

Oil of Cubebs.—This oil is obtained from the fruits of *Piper Cubeba*, a shrub indigenous to Java, Southern Borneo, and Sumatra; it contains according to recent experiments of Oglialore (*Deut. chem. Ges. Ber.*, viii. 1357) a small quantity of a lævorotatory terpene, which boils at 158°—163° (316°·4—325°·4 F.), a lævorotatory hydrocarbon of the composition $C_{15}H_{24}$, and a second hydrocarbon having far less rotatory power but apparently the same composition. The lævorotatory hydrocarbon $C_{15}H_{24}$ boils at 264°—265° (507°·2—509° F.), and at 0° (32° F.) has the sp. gr. 0·9289: it combines with hydrochloric acid, forming a crystalline dihydrochloride, $C_{15}H_{26}Cl_2$; this melts at about 118° (244°·4 F.), and when heated with water to 170°—180° (338°—356° F.), it is decomposed, the original hydrocarbon being separated. The second $C_{15}H_{24}$ hydrocarbon is said to boil at 263°—264° (505°·4—507°·2 F.), but does not combine with hydrochloric acid.

Oil of Cloves.—This oil is obtained from the sun-dried flower buds of the *Eugenia caryophyllata*, an evergreen tree indigenous to the original Moluccas or Clove Islands, but now cultivated in Sumatra, the Mascarene Islands, the islands of Zanzibar and Pemba on the Eastern coast of Africa, the West Indies, &c. Clove oil consists chiefly of *eugenol*, $C_{10}H_{12}O_2$, but contains a relatively small quantity of a lævorotatory $C_{15}H_{24}$ hydrocarbon, and other substances of unknown composition. The hydrocarbon boils almost constantly at 247°[*] (476°·6 F.), and at 15° (59° F.) has the sp. gr. 0·905 (Church, *Journ. Chem. Soc.*, xxviii. 113). It absorbs hydrochloric acid, but the resulting hydrochloride has not been examined.

Oil of Rosewood.—The oil obtained by distilling rosewood with water contains a lævorotatory hydrocarbon of the composition $C_{15}H_{24}$, which boils at 249° (480°·2 F), and readily absorbs hydrochloric acid. (Gladstone.)

Oil of Calamus.—The oil distilled from the root of *Acorus Calamus* consists, according to Kurbatow (*Deut. chem. Ges. Ber.*, vi. 1210), of a terpene, boiling at 158°—159° (316°·4—318°·2 F.), which forms a crystalline hydrochloride, and a $C_{15}H_{24}$ hydrocarbon, which boils at 255°—258° (491°—496°·4 F.), and does not unite with hydrochloric acid.

Oil of Patchouli.—The oil distilled from *Pogostemon Patchouli*, a labiate plant indigenous in the East India Islands, contains, according to Gladstone, a lævorotatory $C_{15}H_{24}$ hydrocarbon boiling at about 257° (494°·6 F.).

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[*] The corrected boiling-point is 253°·9 (487°·4 F.).

Haloid Derivatives of Benzene and its Homologues.

(1307) *Preparation.*—The chloro- and bromo-derivatives of the members of the benzene series are formed, as already stated, by the direct action of chlorine and bromine on the hydrocarbons, but they may also be obtained by another method, which, moreover, is available for the preparation of iodo-derivatives, and which is of special importance, as it enables us to trace the connexion of the haloid compounds with other substitution derivatives. The method in question is commonly spoken of as the method of Griess, the chemist by whom it was introduced. It will be best understood by reference to a special case —the conversion of benzene into chloro-, bromo- and iodobenzene, for example. The hydrocarbon having been converted into the nitro-derivative by the action of nitric acid, is treated with a reducing agent, and thus converted into the amido-derivative (see Amido-derivatives of Benzene, &c.). Now Griess has shown that when the nitrate of the amido-derivative is submitted to the action of nitrous acid, a so-called diazo-compound is produced (the properties of this class of bodies will elsewhere be more fully described), thus:

$$\underset{\text{Amidobenzene nitrate.}}{C_6H_5.NH_3(NO_3)} + HNO_2 = \underset{\text{Diazobenzene nitrate.}}{C_6H_5.N_2(NO_3)} + 2OH_2;$$

and that if this diazobenzene nitrate be then mixed with platinic chloride solution, a double salt of diazobenzene chloride and platinic chloride is precipitated, which furnishes chlorobenzene on distillation with sodic carbonate, being broken up in the following manner:

$$\underset{\text{Diazobenzene platinochloride.}}{2C_6H_5.N_2Cl.PtCl_4} = \underset{\text{Chlorobenzene.}}{2C_6H_5Cl} + N_2 + Pt + 2Cl_2.$$

To obtain bromobenzene, the diazo-nitrate is treated with bromine water, and the resulting *diazobenzene perbromide* is submitted to distillation with sodic carbonate:

$$\underset{\text{Diazobenzene perbromide.}}{C_6H_5.N_2Br_3} = \underset{\text{Bromobenzene.}}{C_6H_5Br} + N_2 + Br_2.$$

The bromo-derivative is usually best prepared, however, by boiling the diazo-perbromide with anhydrous alcohol, or in some cases by the action of a concentrated solution of hydrobromic acid on the diazo-derivative.

The preparation of the iodo-derivative is somewhat easier, as it is merely necessary to convert the diazo-nitrate into the corresponding sulphate, and then warm with a concentrated solution of hydriodic acid:

$$C_6H_5.N_2(HSO_4) + HI = C_6H_5I + N_2 + H_2SO_4.$$

Diazobenzene sulphate. Iodobenzene.

Griess's method, therefore, enables us to displace the NH_2 group by Cl, Br, or I, and therefore the NO_2 group. The method appears to be applicable to all the monamido-derivatives obtained from the nitro-derivatives, but it has not as yet been extended to diamido-derivatives; unfortunately, however, the preparation of the diazo-compounds is often a matter of considerable difficulty, on account of their instability; and in all cases it requires careful and skilful manipulation.

Griess's method also enables us to prepare haloid derivatives of the hydrocarbons of the benzene series from their haloid-amido-derivatives, formed by the action of the halogens on the acetamido-derivatives, or in other words to displace the NH_2 group by hydrogen. For this purpose the nitrate of the haloid amido-derivative is converted into the diazo-nitrate, from which the diazo-sulphate is prepared; and on heating the latter with anhydrous alcohol nitrogen is evolved and the haloid derivative is produced, thus:

$$C_6H_3Br_2.NH_3(NO_3) + HNO_2 = C_6H_3Br_2.N_2(NO_3) + 2OH_2;$$

Dibromamidobenzene nitrate. Dibromodiazobenzene nitrate.

$$C_6H_3Br_2.N_2(HSO_4) + C_2H_5.OH = C_6H_4Br_2 + N_2 + C_2H_4O + H_2SO_4.$$

Dibromodiazobenzene sulphate. Alcohol. Dibromobenzene. Aldehyde.

It is usually, however, sufficient to add the haloid amido-derivative to alcohol saturated with nitrous anhydride, that is to say, to act on it with ethylic nitrite:

$$C_6H_3Br_2.NH_2 + NO_2.C_2H_5 = C_6H_4Br_2 + N_2 + C_2H_4O + OH_2.$$

Dibromamidobenzene. Ethylic nitrite. Dibromobenzene. Aldehyde.

Chloro- and bromo-derivatives of the hydrocarbons of the benzene series are also obtained by distilling phenol and its homologues, and their haloid derivatives, with phosphoric pentachloride or bromide:

$$C_6H_5.OH + PCl_5 = C_6H_5Cl + HCl + POCl_3.$$

Phenol. Chlorobenzene.

Many of the haloid derivatives of the hydrocarbons of the benzene series are oily liquids, whilst the remainder are crystalline solids; they are all insoluble, or nearly so, in water, but soluble in alcohol and many of the ordinary solvents. Excepting those formed by the displacement of hydrogen in the "side chain" they are all extremely stable, the halogen being displaced only with considerable difficulty.

(1308) HALOID DERIVATIVES OF BENZENE.—BENZENE HEXABROMIDE or *Hexabromhexylene:* $C_6H_6Br_6$.—There can be little doubt that the first action of bromine on benzene is to produce the additive compound $C_6H_6Br_2$, but all attempts to isolate this have failed on account of its instability. The additive compound $C_6H_6Br_4$ is also unknown, but the hexabromide $C_6H_6Br_6$ can readily be obtained. To prepare this compound, a mixture of benzene with excess of bromine is exposed to bright sunlight for several days in a large flask; the product is purified by crystallization from ether, from which it separates in minute white rhombic prisms. It is fusible, but is at the same time partially decomposed; when heated with an alcoholic solution of potassic hydrate it furnishes a tribromobenzene.

(1309) BROMOBENZENE or *Phenylic Bromide:* C_6H_5Br.—To prepare this compound a mixture of benzene and bromine in the proportions of their molecular weights (78 : 160) is allowed to stand at the ordinary atmospheric temperature for several days. The bromine does not disappear entirely even after long standing, but at the end of eight or ten days about three-fourths of the benzene is usually converted into bromobenzene, a small quantity of di- and tribromobenzene being also formed. The product, after being washed with a solution of sodic hydrate to remove bromine, and dried with calcic chloride, is submitted to fractional distillation. Pure bromobenzene is a colourless liquid, of pleasant aromatic odour, and is insoluble in water; it boils at 154°—155° (309°·2—311° F.), and at 0° (32° F.) has the sp. gr. 1·517.

(1310) DIBROMOBENZENES: $C_6H_4Br_2$.—Three isomeric modifications of dibromobenzene are known, two of which are produced by the direct action of bromine on benzene. The manner in which Körner has determined their constitution, it will be remembered, has already been described (p. 268).

Paradibromobenzene: $C_6H_4Br_2$, (Br : Br = 1 : 4).—To prepare this body a mixture of one molecule of benzene and rather more than two molecules of bromine is heated on the water-bath in a retort, the neck of which is fused on to the end of a Liebig's condenser, the condenser being so inclined that the condensed vapours of benzene and bromine flow back into the retort. The heating is continued until but little hydrobromic acid is evolved, and the contents of the retort become solid on cooling; the product is then washed with soda, and distilled in a current of steam. The oil which passes over usually deposits a large quantity of crystals on cooling; these are drained from the oil on a vacuum filter, and the latter is cooled in a refrigerating mixture, which causes the separation of a further quantity of crystals. This crude dibromobenzene is then purified by one or two crystallizations from hot alcohol, in which it is readily soluble, although it separates almost entirely on cooling.

Paradibromobenzene may also be prepared from parabromamidobenzene or parabromaniline, $C_6H_4Br.NH_2$, by the method of Griess; or by distilling parabromophenol, $C_6H_4Br.OH$, with phosphoric pentabromide.

Pure paradibromobenzene crystallizes in large colourless monoclinic prisms. According to Körner,* it melts at 89°·3 (192°·7 F.), and boils at 218°·6 (425°·5 F.) under the pressure of 757·6 mm. of mercury at 17°·7 (64° F.), the thermometer stem being entirely immersed in the vapour.

Metadibromobenzene: $C_6H_4Br_2$, (Br : Br = 1 : 3).—This modification has been prepared by Griess's method from metabromaniline or metabromamidobenzene, $C_6H_4Br.NH_2$, and by displacing the NH_2 group by hydrogen in the dibromaniline or dibromamidobenzene, $C_6H_3Br_2.NH_2$, obtained by brominating acetanilid or acetamidobenzene, $C_6H_5.NH.C_2H_3O$, and acting on the resulting dibromacetanilid with potassic hydrate:

$$\underset{\text{Dibromacetamidobenzene.}}{C_6H_3Br_2.NH.C_2H_3O} + KHO = \underset{\text{Dibromamidobenzene.}}{C_6H_3Br_2.NH_2} + \underset{\text{Potassic acetate.}}{KC_2H_3O_2}.$$

It is a colourless liquid, which does not solidify at −28° (−18°·4 F.), of the density 1·955 at 18°·6 (65°·4 F.); it boils, according to Körner, at 219°·4 (426°·9 F.) under the pressure of 754·8 mm. of mercury at 19° (66°·2 F.), the whole of the mercury column of the thermometer being heated by the vapour. Concentrated nitric acid converts it into a mixture of two isomeric nitrodibromobenzenes, $C_6H_3Br_2.NO_2$, one of which melts at 61°·6

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* The original memoir in which all Körner's statements, referred to in the course of the description of the benzene derivatives, are contained is in the *Gazzetta Chimica Italiana*, 1874, p. 305 *et seq.*; an abstract of this memoir is given in the *Journal of the Chemical Society*, vol. xxix. p. 204.

(142°·8 F.), and the other, of which only a very small quantity is formed, melts at 82° (179°·6 F.) (Körner).

Orthodibromobenzene: $C_6H_4Br_2$, (Br : Br=1 : 2).—The oil which drains from the crystals of paradibromobenzene consists chiefly of orthodibromobenzene, although relatively very little of this compound is produced by the action of bromine on benzene, and it also contains additive compounds, which are removed by boiling it for some time with a concentrated alcoholic solution of potassic hydrate; it is then precipitated by water, dried, distilled, and the portion boiling at 213°—216° (415°·4—420°·8 F.) collected apart. In order to free this product from paradibromobenzene, it is cooled in a very carefully-prepared mixture of ice and salt, and the crystals which separate are filtered off on a vacuum filter surrounded with a refrigerating mixture. These operations are repeated several times until a product is obtained from which crystals no longer separate even at −28° (18°·4 F.) (V. Meyer, *Deut. chem. Ges. Ber.*, vii. 1560).

Körner, who has prepared orthodibromobenzene from orthobromamidobenzene by Griess's method, states, however, that it crystallizes when cooled to −6° (21°·2 F.). The product from benzene is said to boil at about 215° (419° F.) (uncorrected); but Körner's product boiled at 223°·8 (179° F.) under the pressure of 751·6 mm. of mercury at 18°·2 (64°·8 F.), the mercury column of the thermometer being immersed in the vapour. Its specific gravity is 2·003 at 0° (32° F.), and 1·977 at 17°·6 (63°·7 F.) (Körner). Concentrated nitric acid converts it into a nitrodibromobenzene, which melts at 57°·8 (136° F.) (Körner). According to V. Meyer (*loc. cit.*), this nitroorthodibromobenzene crystallizes in monoclinic prisms, whereas the isomeric nitrometadibromobenzene melting at 61° (141°·8 F.) crystallizes in triclinic prisms.

(1311) TRIBROMOBENZENES: $C_6H_3Br_3$.—The three isomeric tribromobenzenes which are possible according to Kekulé's hypothesis have been obtained. The manner in which the constitution of these compounds is inferred from their relation to the three isomeric dibromobenzenes has been previously described in connexion with the discussion as to the constitution of the benzene derivatives generally (p. 268).

*Paratribromobenzene:** $C_6H_3Br_3$, (Br : Br : Br=1 : 3 : 5).—

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* It may be laid down as the result of experience, and entirely without reference to any hypothesis as to the relative position of the radicles, that in the

This compound is readily obtained by the action of ethylic nitrite on ordinary tribromaniline, $C_6H_2Br_3.NH_2$ (Stüber, *Deut. chem.*

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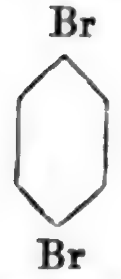
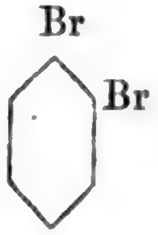
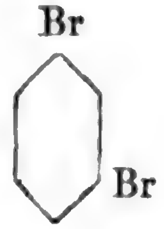
case of the isomeric di-derivatives of benzene, the *para*-di-derivatives are those which, when another atom of hydrogen is displaced, *can only give rise to a single tri-derivative;* whilst the *ortho*-di-derivatives are those which can give rise to *two* isomeric tri-derivatives, and the meta-di-derivatives those which can furnish *three* isomeric tri-derivatives, Similarly, we may call the three series of isomeric tri-derivatives *para-*, *ortho-*, or *meta-* compounds, according as when another atom of hydrogen is displaced, they can give rise to the formation of a *single* tetra-derivative, of *two* isomeric tetra-derivatives, or of *three* isomeric tetra-derivatives. But since, according to Kekulé's hypothesis, the tri-derivatives in which the radicles are relatively in the position 1 : 3 : 5, are those which can only form a single tetra-derivative, they merit the title of *para-* compounds; those tri-derivatives in which the radicles are relatively in the position 1 : 2 : 3 can furnish two isomeric tetra-derivatives, and therefore are the *ortho-* compounds; lastly the 1 : 2 : 4 tri-derivatives can furnish three tetra-derivatives, and hence we may term them *meta-* compounds; thus:



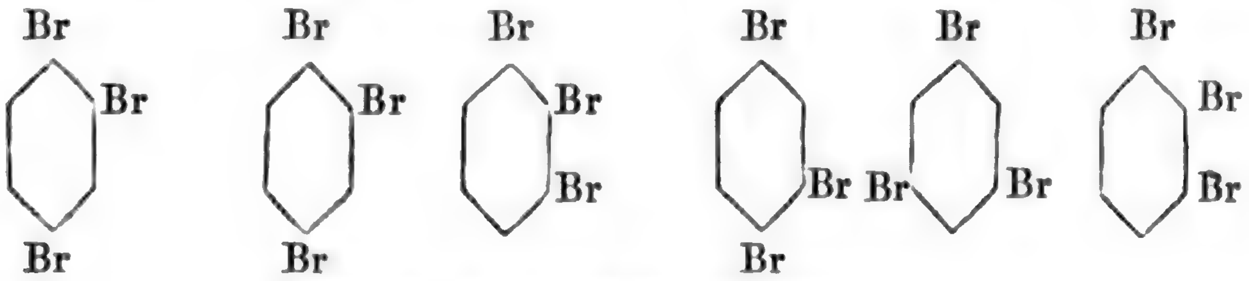
Paradibromobenzene.



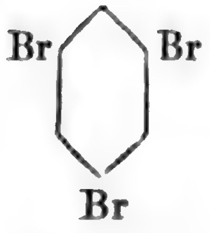
Orthodibromobenzene.



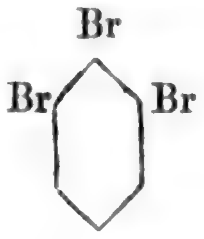
Metadibromobenzene.



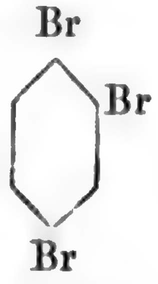
Tribromobenzenes from the three Dibromobenzenes.



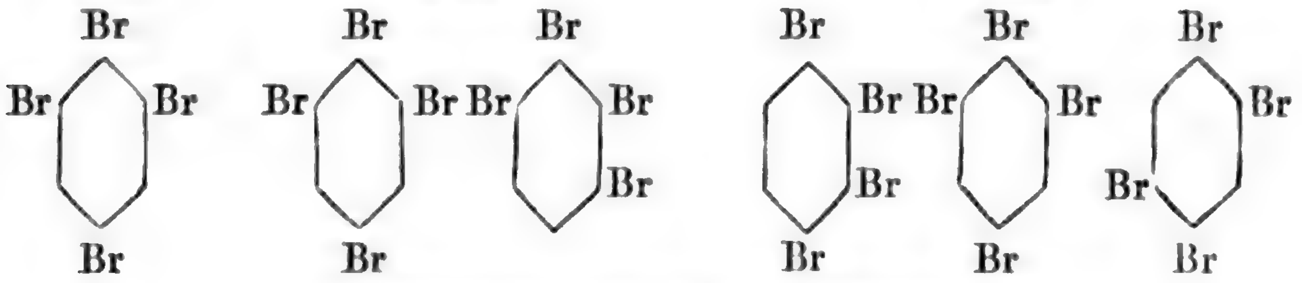
Paratribromobenzene.



Orthotribromobenzene.



Metatribromobenzene.



Tetrabromobenzenes from the three Tribromobenzenes.

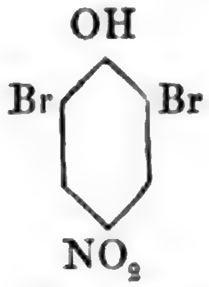
Ges. Ber., iv. 961; Körner). It may also be prepared by Griess's method from the amidometadibromobenzene, which melts at 56°·5 (133°·7 F.) (Körner). Paratribromobenzene crystallizes from alcohol in long needles: it melts at about 119° (246°·2 F.), and boils at about 278° (532°·4 F.) (uncorrected).

Metatribromobenzene: $C_6H_3Br_3$, (Br : Br : Br = 1 : 2 : 4), is the modification which is produced by the action of bromine on benzene, and also when benzene hexabromide is decomposed with potassic hydrate:

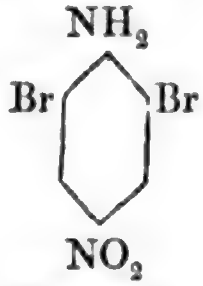
$$\underset{\text{Benzenehexabromide.}}{C_6H_6Br_6} + 3KHO = \underset{\text{Tribromobenzene.}}{C_6H_3Br_3} + 3KBr + 3OH_2.$$

It may be obtained by distilling ordinary dibromophenol, $C_6H_3Br_2.OH$, with phosphoric pentabromide, but it is most readily prepared by Griess's method from ordinary dibromaniline or amido*meta*dibromobenzene, $C_6H_3Br_2.NH_2$, which is converted into the diazo-perbromide, and the latter distilled with a large excess of sodic carbonate (Körner). It is also formed in a similar manner from amido*para* and amido*ortho*dibromobenzene (Körner); and hence since it can be obtained from the three dibromobenzenes there can be no doubt that the bromine atoms occupy the positions 1 : 2 : 4, or which is the same 1 : 3 : 4. Metatribromobenzene crystallizes from alcohol in short needles; it melts at 44° (111°·2 F.), and boils at about 275° (527° F.) (uncorrected).

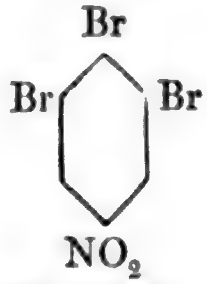
Orthotribromobenzene: $C_6H_3Br_3$, (Br : Br : Br = 1 : 2 : 3).—Körner has obtained this compound by converting dibromoparanitraniline, $C_6H_2Br_2(NO_2).NH_2$, into nitrotribromobenzene, $C_6H_2Br_3.NO_2$, by Griess's method, from which a tribromamidobenzene was then prepared, and the NH_2 group in this compound displaced by hydrogen. The dibromoparanitraniline was obtained from dibromoparanitrophenol, $C_6H_2Br_2(NO_2).OH$, by displacing the OH group by the NH_2 group; and since both the atoms of bromine in this compound are in the ortho-position relatively to the OH group, it follows, that when the OH group is displaced by NH_2, and this in turn by Br, the three atoms of bromine are contiguous, thus:



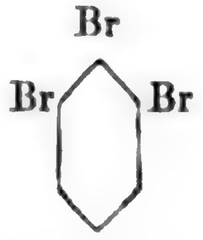
Dibromopara-nitrophenol.



Dibromopara-nitraniline.



Tribromonitro-benzene.



Orthotribromo-benzene.

Orthotribromobenzene crystallizes from alcohol in magnificent rhombic plates; it melts at 87°·4 (189°·3 F.).

(1312) TETRABROMOBENZENES: $C_6H_2Br_4$.—Only two of the three isomeric modifications are known, viz.: (1 : 2 : 3 : 5) *tetrabromobenzene*, which is formed by displacing the NH_2 group in ordinary tribromaniline, $C_6H_2Br_3.NH_2$, by Br by Griess's method (v. Richter, *Deut. chem. Ges. Ber.*, viii. 1428), or by distilling ordinary tribromophenol, $C_6H_2Br_3.OH$, with phosphoric pentabromide; and that obtained by heating paradibromobenzene with excess of bromine to 150° (302° F.) (Riche and Berard), or nitrobenzene with bromine to 250° (482° F.) (Kekulé), in which the bromine atoms probably occupy the positions 1 : 2 : 4 : 5.

Both crystallize from alcohol in white needles; the former melts at 98°·5 (209°·3 F.), and the latter, according to Kekulé, at 137°—140° (278°·6—284° F.).

(1313) PENTABROMOBENZENE: C_6HBr_5.—Kekulé obtained this compound in small quantity together with tetrabromobenzene, by heating nitrobenzene with bromine to 250° (482° F.). It is almost insoluble in alcohol, but sublimes readily in needles which do not melt below 240° (464° F.).

Hexabromobenzene has not been prepared.

(1314) BENZENE HEXACHLORIDE, or *Hexachlorhexylene*: $C_6H_6Cl_6$.—Chlorine has scarcely any action on cold benzene in the dark, but according to H. Müller (*Jahresber. Chem.*, 1862, 414) when chlorine acts on boiling benzene even in darkness a mixture of the three additive compounds, $C_6H_6Cl_2$, $C_6H_6Cl_4$, and $C_6H_6Cl_6$, is slowly produced, and but very little substitution product is obtained. The only additive compound which has been isolated and described, however, is the hexachloride. This body is formed by passing chlorine into boiling benzene, or by introducing benzene into a large white glass flask or bottle filled with chlorine, and exposing the mixture to sunlight. The former appears to be the easier method, although a very great deal of the chlorine escapes without acting on the benzene: the unattacked benzene is distilled off, and the crystals which separate on cooling are recrystallized from benzene.

Benzene hexachloride crystallizes from benzene in large transparent colourless monoclinic prisms; it melts at 157° (314°·6 F.) (Heys, *Zeits. Chem.* [2], vii. 293). It is not in the least affected by boiling with fuming nitric acid, or a mixture of concentrated sulphuric and fuming nitric acids (Heys). When heated with an alcoholic solution of potassic hydrate, it is readily converted into trichlorobenzene.

(1315) CHLOROBENZENE, or *Phenylic Chloride*: C_6H_5Cl.—In presence of such substances as iodine, molybdenic pentachloride, or antimonic pentachloride, chlorine acts rapidly on benzene. The use of iodine and of antimonic pentachloride was first noticed by H. Müller (*loc. cit.*), and by the aid of the former Jungfleisch has prepared a complete series of chlorinated benzenes. The employment of molybdenic pentachloride has recently been introduced by Aronheim (*Deut. chem. Ges. Ber.*, viii. 1400). Iodine and molybdenic pentachloride are less energetic reagents than antimonic pentachloride, and are therefore to be chosen when the lower derivatives are required.

When chlorine is passed into benzene containing iodine in solution, chlorobenzene is first formed, then dichlorobenzene; and it is only necessary to heat the mixture gently at first, after which the action goes on by itself. When the greater part is converted into dichlorobenzene, the mass solidifies on cooling; but on continuing the passage of the chlorine, it becomes liquid again owing to the formation of trichlorobenzene. As the change into tetrachlorobenzene takes place the mass again solidifies, and it is necessary to heat more strongly during the conversion of the tetra- into pentachlorobenzene, although when the latter is produced the mass becomes more fusible. It is not easy to prepare hexachlorobenzene in this manner, owing to the comparatively high temperature required, and the consequent loss of iodine by volatilization.

All the chloro-derivatives of benzene are thus formed in rapid succession, and after a certain time a greater or less amount of each appears to be present in the product, although one of them always predominates, so that by stopping the action at certain stages we may isolate any one of the desired bodies. Small quantities of iodobenzenes are also present in the mixture; but by exposure to sunlight or by distillation, these are decomposed with liberation of iodine, which may then be removed by treatment with potassic hydrate.

To prepare chlorobenzene, chlorine is passed into benzene mixed with iodine, the mixture being gently heated at first, after which the action goes on by itself. The liquid is distilled from time to time, and the portion boiling above 130° (266° F.) set aside, the portion boiling below this temperature being again submitted to the action of the chlorine. When a sufficient quantity of crude chlorobenzene has been obtained, it is first purified by alternate agitation with potassic hydrate solution, and exposure for several days to sunshine, which causes the decomposition of the small quantities of iodobenzenes present, and finally fractionally distilled.

Chlorobenzene is also produced when phenol is distilled with phosphoric pentachloride:

$$\underset{\text{Phenol.}}{4C_6H_5.OH} + PCl_5 = \underset{\text{Chlorobenzene.}}{C_4H_5Cl} + \underset{\text{Phenylic phosphate.}}{PO(OC_6H_5)_3} + 4HCl.$$

According to Jungfleisch (*Ann. Ch. Phys.* [4], xv. 212) chlorobenzene is a limpid colourless, highly refractive liquid of sp. gr. 1·1293 at 0° (32° F.), 1·1169 at 10° (50° F.), and 1·1088 at 20° (68° F.); it boils at 133° (271°·4 F.). When cooled in a mixture of solid carbonic anhydride and ether it solidifies to a crystalline mass, which becomes liquid at about −40° (−40° F.). It is not in the least affected when heated to 200° (392° F.) in sealed tubes with an alcoholic solution of potassic hydrate.

Iron, copper, zinc, and tin do not act appreciably on chlorobenzene even at 250° (482° F.), and it is not attacked by potassium or sodium in the cold, although it furnishes *diphenyl*, $C_{12}H_{10}$, when heated with these metals.

Chlorine has little action on chlorobenzene in the dark, but when the mixture is exposed to sunlight rapid action takes place, and the additive compounds, $C_6H_5Cl_3$, $C_6H_5Cl_5$, $C_6H_5Cl_7$, and perhaps $C_6H_5Cl_9$, are formed; if a large excess of chlorine be employed, higher chlorinated compounds are also produced, such as $C_6H_4Cl_4$, $C_6H_4Cl_6$, and $C_6H_4Cl_8$ (Jungfleisch). The only one of these that has been obtained in a state of purity is the compound $C_6H_4Cl_8$, which crystallizes from chloroform in small oblique rhombic prisms; it does not fuse below 250° (482° F.), but undergoes partial decomposition even below that temperature; when treated with an alcoholic solution of potassic hydrate it furnishes pentachlorobenzene:

$$C_6H_4Cl_8 + 3KHO = C_6HCl_5 + 3KCl + 3OH_2.$$

(1316) **DICHLOROBENZENES**: $C_6H_4Cl_2$.—The continued action of chlorine on benzene in presence of iodine results chiefly in the formation of *para*dichlorobenzene, but a small quantity of *ortho*dichlorobenzene is also produced.

Paradichlorobenzene: $C_6H_4Cl_2$, (Cl : Cl = 1 : 4).—This compound may be prepared by passing chlorine into a solution of iodine in benzene until the liquid partly solidifies in the crystalline state on cooling; but the method which is perhaps preferable is to employ benzene mixed with about one per cent. of its weight of molybdenic pentachloride. The mixture is gently heated, and chlorine passed until the increase of weight is about that required by theory. On cooling the product, a large quantity of crystals separate, which are drained, pressed, distilled, and finally crystallized from alcohol. A further quantity of solid dichlorobenzene may be obtained by fractionally distilling the liquid which drains from the crystals, and cooling the distillates (Aronheim, *loc. cit.*).

Paradichlorobenzene is also obtained by distilling parachlorophenol, $C_6H_4Cl.OH$, with phosphoric pentachloride, and by Griess's method from parachloramidobenzene or parachloraniline.

Paradichlorobenzene crystallizes from ether in large right rhombic prisms; from hot alcohol, in which it is very soluble, it separates in much smaller crystals; it readily sublimes even at the ordinary temperature. According to Körner, it melts at 56°·4 (133°·5 F.), and boils at 173° (343°·4 F.); but according to Jungfleisch, it melts at 53° (127°·4 F.), and boils at 171° (339°·8 F.). When exposed to sunlight, in presence of chlorine, it furnishes a mixture of additive compounds, only one of which ($C_6H_4Cl_8$), however, has been isolated (Jungfleisch).

Metadichlorobenzene: $C_6H_4Cl_2$, (Cl : Cl = 1 : 3), prepared by Griess's method from metachloramidobenzene, $C_6H_4Cl.NH_2$, is a colourless liquid which boils at 172° (341°6 F.); it does not solidify in a mixture of ice and salt (Körner).

Orthodichlorobenzene: $C_6H_4Cl_2$, (Cl : Cl = 1 : 2).—This modification is produced by distilling orthochlorophenol, $C_6H_4Cl.OH$, with phosphoric pentachloride, and together with paradichlorobenzene by the action of chlorine on benzene. To obtain it pure from the latter source, the oil boiling at 175°—185° (347°—365° F.) is separated as far as possible from the para-compound by cooling, and is then warmed with moderately strong fuming sulphuric acid on the water-bath: the paradichlorobenzene which it contains is not acted upon by the acid under these circumstances, but the isomeride is converted into a *sulpho-acid*, $C_6H_3Cl_2.HSO_3$, and on pouring the mixture into water, the latter dissolves, the paradichlorobenzene remaining undissolved. The solution is then treated with baric carbonate, the baric salt of the sulpho-acid decomposed with the necessary quantity of sulphuric acid, and the solution evaporated to dryness: when the sulpho-acid thus obtained is distilled from the oil-bath, pure orthodichlorobenzene passes over (Beilstein and Kuhlberg, *Deut. chem. Ges. Ber.*, vii. 1759). It is a colourless liquid, which boils at 179° (354°·2 F.).

Jungfleisch only noticed the formation of a single dichlorobenzene from benzene, and he also obtained only one tri- and one tetrachlorobenzene; but on decomposing with potassic hydrate the mixture of additive compounds formed from chlorobenzene by an excess of chlorine, a product was obtained containing small quantities of chlorobenzenes identical with those formed directly from benzene, together with isomeric bodies of much lower melting-point. As these compounds do not appear to have been prepared in a state of purity, owing to the small quantity which was produced, we have no reliable information as to their nature.

(1317) TRICHLOROBENZENES: $C_6H_3Cl_3$.—*Paratrichlorobenzene* (Cl : Cl : Cl = 1 : 3 : 5), obtained by Griess's method from ordinary trichloraniline, $C_6H_2Cl_3.NH_2$, closely resembles the corresponding tribromobenzene; it crystallizes in long needles, which melt at 63°·4 (146°·1 F.) (Körner).

Metatrichlorobenzene: $C_6H_3Cl_3$, (Cl : Cl : Cl = 1 : 2 : 4).—The trichlorobenzene obtained by chlorinating benzene, or by acting on benzene hexachloride with potassic hydrate, appears to be this modification. It crystallizes in large right rhombic prisms, and melts at 17° (62°·6 F.); it boils at 206° (402°·8 F.). When exposed to sunlight in presence of chlorine it furnishes a series of crystalline additive compounds (Jungfleisch).

Jungfleisch obtained an isomeric trichlorobenzene melting at about 60° (140° F.) from the oily product of the decomposition of the additive chloro-compounds of chlorobenzene with potassic hydrate. Judging from its melting point it appears probable that this body is paratrichlorobenzene.

(1318) TETRACHLOROBENZENE: $C_6H_2Cl_4$.—The product obtained by passing chlorine into a solution of iodine in benzene until the mixture boils at about 220° (428° F.) consists chiefly of a tetrachlorobenzene in which the chlorine atoms probably occupy the portions 1 : 2 : 4 : 5. It crystallizes in rhombic prisms which melt at 139° (282°·2 F.), and it boils at 240° (464° F.). It slowly combines with chlorine in the sunlight, forming an oily product.

Jungfleisch and Otto (*Ann. Chem. Pharm.*, cxl. 104) have described an isomeric tetrachlorobenzene melting at 35° (95° F.) and boiling at about 253° (487°·4 F.), obtained from the additive chloro-compounds of chlorobenzene. It crystallizes in long needles and is readily soluble in hot alcohol, which dissolves the isomeric body very sparingly.

Ladenburg has also noticed the formation from chlorobenzene in this manner of a tetrachlorobenzene of low melting point (*Deut. chem. Ges. Ber.*, v. 789).

A third tetrachlorobenzene (1 : 2 : 4 : 6) is obtained by the action of phosphoric pentachloride on trichlorophenol; it crystallizes in short needles, and melts at 45° (113° F.).

(1319) PENTACHLOROBENZENE: C_6HCl_5.—The product which boils at about 260° (500° F.) obtained by the continued action of chlorine on benzene in presence of iodine consists chiefly of a mixture of penta- and hexachlorobenzene. In order to separate these, the mixture is treated with boiling alcohol: the former being much more soluble dissolves, and the crude pentachlorobenzene is then several times recrystallized from benzene. Pentachlorobenzene, which crystallizes from alcohol in fine needles, melts at 74° (165°·2 F.), and boils at 272° (521°·6 F.). When exposed to sunlight with chlorine, it is very slowly converted into an oily substance without any evolution of hydrochloric acid.

Jungfleisch and Otto state that an isomeric body of higher melting point may be obtained by treating the chloro- additive compounds of chlorobenzene with potassic hydrate; their experiments have been repeated by Ladenburg, however, who has shown that the supposed isomeric pentachlorobenzene is nothing more than impure hexachlorobenzene (*loc. cit.*, and *ibid.* vi. 32). Ladenburg finds the melting point of pentachlorobenzene to be 85°—86° (185°—186°·8 F.), and its boiling point 275°—277° (527°—530°·6 F.).

(1320) HEXACHLOROBENZENE: C_6Cl_6.—This compound is the final product of the action of chlorine on benzene in presence of iodine, $SbCl_5$, &c., and also of the action of chloride of iodine on the homologues of benzene; it is also formed by passing chloroform vapour through a red-hot tube (Bassett, *Journ. Chem. Soc.* [2], v. 443), and by heating tetrachlorethane or acetylene tetrachloride, $C_2H_2Cl_4$, in sealed tubes to 300° (572° F.) for 15 hours (Berthelot):

$$C_2H_2Cl_4 = 2HCl + C_2Cl_2 \quad ; \quad 3C_2Cl_2 = C_6Cl_6.$$

Tetrachlorethane. Dichloracetylene. Dichloracetylene. Hexachlorobenzene.

It is most readily prepared by passing chlorine into a mixture of benzene with antimonic pentachloride until hydrochloric acid is no longer evolved. The product is then treated with concentrated hydrochloric acid to remove the antimony compound, washed with water, dried, extracted with boiling alcohol, and finally crystallized from a mixture of alcohol and benzene. It forms long, slender, silky needles of dazzling whiteness; it melts at 226° (438°·8 F.), and boils at 326° (618°·8 F.) (corr.)* It does not appear to unite with chlorine in sunshine (Jungfleisch); and it is not in the least affected when boiled with an alcoholic solution of potassic hydrate.

(1321) FLUORBENZENE: C_6H_5F.—This compound, which is the only fluorine derivative of a hydrocarbon yet investigated, is obtained by distilling the calcic salt of fluorbenzoic acid with about four times its weight of calcic hydrate:

$$(C_6H_4\,F.\,CO_2)_2Ca + Ca(OH)_2 = 2C_6H_5\,F + 2CaCO_3.$$

Calcic fluorbenzoate. Fluorbenzene.

It is purified by fractional distillation. Fluorbenzene crystallizes in scales which melt at 40° (104° F.); it boils at 180°—183° (356°—361°·4 F.). It is insoluble in water, but readily soluble in alcohol or ether (Schmitt and Gehren, *Journ. pr. Chem.* [2], i. 400).

(1322) IODOBENZENE or *phenylic iodide:* C_6H_5I.—Iodobenzene cannot be prepared by the action of iodine on benzene, but when benzene is heated with iodine and iodic acid in sealed tubes to 200°—240° (392°—464° F.) a mixture of iodobenzene and di- and tri-iodobenzene is produced (Kekulé); the tubes should be opened from time to time in order to permit the escape of the carbonic anhydride resulting from secondary reaction. The non-formation of iodobenzene by the action of iodine alone, is due to the reconversion of this compound into benzene by the hydriodic acid generated in its formation from benzene and iodine, thus:

$$C_6H_6 + I_2 = C_6H_5I + HI \quad ; \quad C_6H_5I + HI = C_6H_6 + I_2.$$

Benzene. Iodobenzene. Iodobenzene. Benzene.

When iodic acid is present, however, the hydriodic is removed from the sphere of action as soon as it is formed, and the iodobenzene no longer undergoes reduction:

$$C_6H_6 + 2I_2 + HIO_3 = 5C_6H_5I + 3OH_2.$$

Iodobenzene is most conveniently prepared by Griess's method by the action of hydriodic acid on diazobenzene sulphate from amidobenzene or aniline, $C_6H_5.NH_2$:

$$C_6H_5.N_2(HSO_4) + HI = C_6H_5I + N_2 + H_2SO_4.$$

Diazobenzene sulphate. Iodobenzene.

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* The boiling point determined with Berthelot's air thermometer was 332° (629°·6 F.); Bassett mentions 331° (627°·8 F.) as the corrected boiling point of hexachlorobenzene.

It is also formed by the action of iodide of phosphorus on phenol, and by the action of iodine chloride on sodic benzoate:

$$\underset{\text{Sodic benzoate.}}{C_6H_5.CO_2Na} + ICl = \underset{\text{Iodine benzoate.}}{C_6H_5.CO_2I} + NaCl.$$

$$\underset{\text{Iodine benzoate.}}{C_6H_5.CO_2I} = \underset{\text{Iodobenzene.}}{C_6H_5I} + CO_2.$$

It is a colourless liquid, having an odour similar to that of benzene and phenol, and does not solidify at − 18° (− 0°·4 F.). Its sp. gr. at 15° (59° F.) is 1·833, and it boils at 185° (365° F.). It is easily converted into benzene by the action of sodium amalgam and water, or by heating it with aqueous hydriodic acid to 250° (482° F.), but it is not acted on by potassic hydrate.

(1323) **Diiodobenzenes.** *Paradiiodobenzene:* $C_6H_4I_2$, (I : I = 1 : 4).—This compound is formed together with iodo- and tri-iodobenzene when benzene is heated with iodine and iodic acid, and by Griess's method from paramidoiodobenzene, $C_6H_4I.NH_2$. It crystallizes in laminæ which melt at 129°·4 (264°·9 F.), and resemble naphthalene in appearance (Körner).

Metadiiodobenzene: $C_6H_4I_2$, (I : I = 1 : 3), prepared from metamidoiodobenzene by Griess's method resembles the para-compound; it melts at 40°·5 (104°·9 F.), and boils at 285° (545° F.) (Körner).

Orthodiiodobenzene: $C_6H_4I_2$, (I : I = 1 : 2), from orthamidoiodobenzene, is a crystalline solid, and boils at a higher temperature than its isomerides (Körner).

(1324) **Triiodobenzene:** $C_6H_3I_3$.—The only known modification of this compound is that obtained together with iodo- and diiodobenzene on heating benzene with iodine and iodic acid; it forms small needles, which melt at 76° (168°·8 F.) (Kekulé).

(1325) **Chlorobromobenzene.** *Parachlorobromobenzene:* C_6H_4BrCl (Br : Cl = 1 : 4).—This compound is formed by heating chlorobenzene on the water-bath with an excess of bromine until the product solidifies on cooling, and by Griess's method from parachlor- and parabromamidobenzene. It resembles paradibromobenzene, but melts at 67°·4 (153°·3 F.) and boils at 196°·3 (385°·3 F.) (Körner).

(1326) **Bromiodobenzenes:** C_6H_4BrI.—Körner has prepared the three isomeric bromiodobenzenes from the three bromamidobenzenes by Griess's method.

Parabromiodobenzene (Br : I = 1 : 4) crystallizes in plates and prisms like paradibromobenzene; it melts at 92° (197°·6 F.), and boils at 251°·5 (484°·7 F.).

Metabromiodobenzene (Br : I = 1 : 3) is a colourless liquid which boils at 252° (485°·6 F.).

Orthobromiodobenzene (Br : I = 1 : 2) is also a colourless liquid, but boils at 257°·5 (495°·5 F.).

(1327) **Chloriodobenzenes:** C_6H_4ICl.—*Parachloriodobenzene* (Cl : I = 1 : 4) from parachloramidobenzene, is a crystalline solid; it boils at 227°·6 (441°·6 F.) under the pressure of 751·2 mm. of mercury at 27° (80·6 F.) (Körner).

Orthochloriodobenzene (Cl : I = 1 : 2), from orthochloramidobenzene, is a liquid boiling above 233° (451°·4 F.) (Körner).

(1328) **Chloro-derivatives of Toluene.**—It has already been pointed out that the action of chlorine on the homologues of benzene causes the displacement of the hydrogen in the C_6 group when the hydrocarbon is well cooled, and a similar result is obtained, especially in presence of iodine, and molybdenic or antimonic pentachlorides, even if the hydrocarbon be heated. When chlorine acts upon the boiling hydrocarbon, however, the reaction is different, only the hydrogen in the side chain being displaced.

To prepare the former class of derivatives, a small quantity of iodine or molybdenic pentachloride* is added to toluene, and the mixture gently heated, whilst chlorine is passed into it until about the theoretical amount has been employed; this may readily be ascertained by connecting an apparatus for absorbing the hydrochloric acid produced, to the other end of the condenser to which the flask containing the mixture is attached; the flask and the absorption apparatus being weighed together from time to time. The product is then fractionally distilled, and the portion which boils lower than the derivative which is being prepared again submitted to the action of chlorine, whilst the portion of higher boiling point may be employed in the preparation of higher chlorinated derivatives. By this means, the formation of those derivatives in which the hydrogen in the side chain is displaced is entirely avoided, although they may readily be prepared in a similar manner by merely passing the chlorine into pure *boiling* toluene, taking care to avoid the use of iodine or metallic chlorides.

We are chiefly indebted to Beilstein and Kuhlberg and to Limpricht for our knowledge of these compounds, which will be found described at length in the following papers:—Limpricht, *Ann. Chem. Pharm.*, cxxxix. 303; Beilstein and Geitner, *ibid.* cxxxix. 331; Beilstein and Kuhlberg, *ibid.* cxlvi. 317; cl. 286; clii. 224 and 247; clxxix. 282.

The various chlorotoluenes may be represented in a very simple manner as suggested by Beilstein and Kuhlberg, by indicating by figures placed before their names the number of atoms of hydrogen displaced by chlorine, either in the C_6H_5 or the CH_3 group of toluene, or in both groups. Thus we may distinguish the three dichlorotoluenes represented by the formulæ:

$$C_6H_3Cl_2.CH_3 \;;\; C_6H_4Cl.CH_2Cl \;;\; C_6H_5.CHCl$$

as (2–0) dichlorotoluene, (1–1) dichlorotoluene, and (0–2) dichlorotoluene respectively. If it be desired to give systematic names to the chlorotoluenes, the first of these compounds may be termed *methyldichlorobenzene*, the second *chloromethylchlorobenzene*, and the third *dichloromethylbenzene*.

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* Although this substance has not been much used hitherto, it is probably to be preferred, for when iodine is employed, small quantities of iodo-derivatives are formed which can only be removed with extreme difficulty.

(1329) MONOCHLOROTOLUENES. — (1–0) *Chlorotoluenes* or *Methylchlorobenzenes:* $C_6H_4Cl.CH_3$.—The first product of the action of chlorine on toluene in presence of iodine consists chiefly of *parachlorotoluene* ($CH_3 : Cl = 1 : 4$), but *orthochlorotoluene* is also produced: the mixture of these bodies boils at 158°—161° (316°·4—321°·8 F.), and has at 27° (80°·6 F.) the sp. gr. 1·073. It is not known whether metachlorotoluene ($CH_3 : Cl = 1 : 3$) is also formed. Pure parachlorotoluene obtained by Griess's reaction from paramidotoluene or paratoluidine, $C_6H_4(NH_2)CH_3$, is a white crystalline substance, melting at 6°·5 (43°·7 F.), which boils at 160°·5 (320°·9 F.); it furnishes parachlorobenzoic acid, $C_6H_4Cl.COOH$, on oxidation (Huebner and Majert, *Deut. chem. Ges. Ber.*, vi. 790). Metachlorotoluene similarly prepared from metatoluidine is a liquid which boils at 156° (312°·8 F.), and yields metachlorobenzoic acid on oxidation (Wroblevsky, *Ann. Chem. Pharm.*, clxviii. 147). Potassic cyanide, acetate, or sulphide, and also silver salts are entirely without action on these chlorotoluenes.

(0–1) *Chlorotoluene, Chloromethylbenzene* or *Benzylic chloride:* $C_6H_5.CH_2Cl$, which is the first product of the action of chlorine on heated toluene,* is also formed by the action of hydrochloric acid on benzylic alcohol, $C_6H_5.CH_2(OH)$. It is a colourless mobile liquid, the vapour of which produces a peculiar irritation of the eyes, causing a flow of tears, whereas the (1–0) chlorotoluenes have no such action. It boils at 176° (348°·8 F.), and also has a higher specific gravity than (1–0) chlorotoluene. On oxidation it is converted into benzoic acid, $C_6H_5.COOH$, being far more readily oxidized than its isomerides; it is also decomposed when heated with water, sodic ethylate, alcoholic ammonia solution, or potassic cyanide or sulphide in alcoholic solution. Benzylic chloride, in fact, closely resembles the monochlorinated paraffins, entering into reactions of double decomposition, and, like them, being convertible into the corresponding alcohol.

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* When chlorine is passed into toluene the action at once commences, and much heat is evolved, so that if the current of gas be rapid the hydrocarbon is even caused to boil; the product consists almost entirely of benzylic chloride. In presence of iodine, however, the action is comparatively sluggish, the (1–0) chlorotoluenes being much less readily formed than benzylic chloride.

(1330) DICHLOROTOLUENES.—Theoretically several isomeric modifications of the dichlorotoluenes, $C_6H_3Cl_2.CH_3$ and $C_6H_4Cl.CH_2Cl$, can exist, in addition to the compound $C_6H_5.CHCl_2$, but they have been only imperfectly examined.

(2–0) *Dichlorotoluene. Methyldichlorobenzene:* $C_6H_3Cl_2.CH_3$, formed by the action of chlorine on toluene mixed with iodine, boils at 196°—198°, and is undoubtedly a mixture of isomeric (2–0) dichlorotoluenes; it appears, however, to contain the modification $CH_3 : Cl : Cl = 1 : 3 : 4$, since on oxidation it furnishes a dichlorobenzoic acid, $C_6H_3Cl_2.COOH$, melting at 201° (393°·8 F.), identical with that obtained by chlorinating benzoic acid, and also formed on chlorinating *para-* and *meta*chlorobenzoic acid (Beilstein and Kuhlberg). (2–0) Dichlorotoluene is oxidized with very great difficulty, however, and in order to prepare dichlorobenzoic acid from it, it is better to convert it into the compound $C_6H_3Cl_2.CCl_3$ by passing chlorine into the boiling dichlorotoluene as long as any action takes place; the product is then purified by fractional distillation, and heated with water in sealed tubes to 200° (392° F.), whereby it is completely decomposed in the following manner:

$$C_6H_3Cl_2.CCl_3 \ + \ 2OH_2 \ = \ C_6H_3Cl_2.COOH \ + 3HCl.$$

The compound $C_6H_3Cl_2.CCl_3$ thus obtained by Beilstein and Kuhlberg boiled at 273° (523°·4 F.). By acting on the dichlorotoluene formed in presence of molybdenic pentachloride with chlorine, Aronheim and Dietrich (*Deut. chem. Ges. Ber.*, viii. 1401) have obtained a compound having similar properties, but they also isolated by fractional distillation an isomeric substance boiling at about 280° (536° F.), which on decomposition with water furnished a dichlorobenzoic acid melting at 122° (251°·6 F.), which is perhaps derived from the (2–0) dichlorotoluene $CH_3 : Cl : Cl = 1 : 2 : 4$.

(1–1) *Dichlorotoluene. Chloromethylchlorobenzene:* $C_6H_4Cl.CH_2Cl$.—This compound may be obtained either by the action of chlorine on boiling (1–0) chlorotoluene or by its action on benzylic chloride in presence of iodine; the product when purified by fractional distillation boils at 213°—214° (415°·4—417°·2 F.). Its vapour, like that of benzylic chloride, has an irritating action on the eyes. It furnishes parachlorobenzoic acid, $C_6H_4Cl.COOH$, on oxidation, and one of the atoms of chlorine may be readily displaced by other radicles such as CN, HS, &c., by the action of alcoholic solutions of potassic cyanide or sulphydrate. Inasmuch as the action of chlorine on toluene in presence of iodine produces a mixture of (1–0) chlorotoluenes—although the product consists chiefly of parachlorotoluene—there can be little doubt that isomeric bodies of the composition $C_6H_4Cl.CH_2Cl$ are also formed, parachlorobenzylic chloride ($CH_2Cl : Cl = 1 : 4$) being merely the chief constituent of the product.

(0–2) *Dichlorotoluene. Dichloromethylbenzene:* $C_6H_5.CHCl_2$.—This body is the second product of the action of chlorine on boiling toluene; it is also formed from benzoic aldehyde in the following manner:

$$C_6H_5.COH \ + \ PCl_5 \ = \ C_6H_5.CHCl_2 \ + \ POCl_3 \ + \ HCl.$$

Benzoic aldehyde. (0-2) Dichlorotoluene.

It is a colourless liquid of faint odour, which boils at about 206° (402°·8 F.); when heated with water to 150° (302° F.) it furnishes benzoic aldehyde. It also enters into reactions of double decomposition, being converted by the action of argentic acetate, for example, into the compound $C_6H_5.CH(C_2H_3O_2)_2$. By the action of oxidizing agents it is converted into benzoic acid.

(1331) TRICHLOROTOLUENES.—The displacement of three atoms of hydrogen in toluene may be effected in such a manner as to produce the following bodies:

$$C_6H_2Cl_3.CH_3 \ ; \ C_6H_3Cl_2.CH_2Cl \ ; \ C_6H_4Cl.CHCl_2 \ ; \ C_6H_5.CCl_3.$$

Moreover, isomeric modifications of each of these, excepting the last, are possible.

(3–0) *Trichlorotoluene. Methyltrichlorobenzene*: $C_6H_2Cl_3.CH_3$.—This compound is produced with the greatest readiness when chlorine is passed into toluene mixed with iodine, until the weight of 100 parts of the hydrocarbon is increased to 212·5 parts; the product is then shaken up with potassic hydrate solution, dried, and fractionally distilled. The portion which passes over at 235°—240° (455°—464° F.), either solidifies spontaneously, or when cooled with ice; it is separated from the liquid portion by pressing, and then crystallized from alcohol. (3–0) Trichlorotoluene crystallizes in brilliant prisms; it melts at 76° (168·8 F.), and boils at 237°(458°·6 F.) (Limpricht, *ibid.* cxxxix. 326). On oxidation it is slowly converted into a trichlorobenzoic acid, $C_6H_2Cl_3.COOH$, melting at 163° (325°·4 F.), which is identical with that obtained by chlorinating benzoic acid; this acid is more readily obtained by acting on the boiling (3–0) trichlorotoluene with chlorine and heating the resulting compound, $C_6H_2Cl_3.CCl_3$, with water to 260° (500° F.). Aronheim and Dietrich have noticed the simultaneous formation of a liquid trichlorotoluene from toluene, by the action of chlorine in presence of molybdenic pentachloride.

(2–1) *Trichlorotoluene. Chloromethyldichlorobenzene*: $C_6H_3Cl_2.CH_2Cl$.—To obtain this compound benzylic chloride to which iodine is added, or boiling (2–0) dichlorotoluene, is submitted to the action of chlorine. It is a liquid which boils at 241° (465°·8 F.). One of the atoms of chlorine may be readily displaced: thus by the action of potassic acetate it is converted into the compound $C_6H_3Cl_2.CH_2(C_2H_3O_2)$.

(1–2) *Trichlorotoluene. Dichloromethylchlorobenzene*: $C_6H_4Cl.CHCl_2$.—This body is prepared by the action of chlorine on boiling chlorotoluene, or on (0–2) dichlorotoluene, $C_6H_5.CHCl_2$, in presence of iodine. It is a liquid which boils constantly at 234° (453°·2 F.); when heated with water to 170° (338° F.) it is completely converted into hydrochloric acid and parachlorobenzoic aldehyde:

$$C_6H_4Cl.CHCl_2 + OH_2 = C_6H_4Cl.COH + 2HCl.$$

On oxidation it furnishes parachlorobenzoic acid.

(0–3) *Trichlorotoluene. Trichloromethylbenzene*: $C_6H_5.CCl_3$.—This compound is obtained with the greatest readiness by passing chlorine into boiling toluene until no further increase of weight takes place; it is also formed by heating benzoic chloride with phosphoric pentachloride to 180° (356° F.) in sealed tubes:

$$\underset{\text{Benzoic chloride.}}{C_6H_5.COCl} + PCl_5 = \underset{\text{(0–3) Trichlorotoluene.}}{C_6H_5.CCl_3} + POCl_3.$$

It is a colourless liquid which boils at about 214° (417°·2 F.); it is only slightly acted upon by water at about 100° (212° F.), but when heated with it to 150° (302° F.) it is completely converted into benzoic acid and hydrochloric acid:

$$\underset{\text{(0–3) Trichlorotoluene.}}{C_6H_5.CCl_3} + 2OH_2 = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + 3HCl.$$

It is not acted upon by sodium at its boiling point, but when digested with sodic ethylate at 100°(212° F.) it is converted into the compound $C_6H_5.C(OC_2H_5)_3$. Chlorine appears to be entirely without action upon it even at its boiling point, but when a small quantity of iodine is present the hydrogen in the C_6 group becomes displaced.

(1332) TETRACHLOROTOLUENES.—The following modifications of tetrachlorotoluene have been obtained :

$$C_6HCl_4.CH_3 \quad ; \quad C_6H_2Cl_3.CH_2Cl \quad ; \quad C_6H_3Cl_2.CHCl_2 \quad ; \quad C_6H_4Cl.CCl_3.$$

(4–0) *Tetrachlorotoluene. Methyltetrachlorobenzene:* $C_6HCl_4.CH_3$.—This compound is formed together with more or less pentachlorotoluene (5–0) when toluene is treated with chlorine in presence of iodine until no further absorption of chlorine takes place. It crystallizes in needles which melt at 91° (195°·8 F.), and it boils at 271° (519°·8 F.).

(3–1) *Tetrachlorotoluene. Chloromethyltrichlorobenzene:* $C_6H_2Cl_3.CH_2Cl$.—This substance is prepared by passing chlorine into boiling (3–0) trichlorotoluene. It is a liquid which does not solidify at – 20° (–4° F.), and boils constantly at 273° (523°·4 F.). It readily exchanges one atom of chlorine for other radicles: thus when boiled with an alcoholic solution of potassic acetate it furnishes the compound $C_6H_2Cl_3.CH_2(C_2H_3O_2)$.

(2–2) *Tetrachlorotoluene. Dichloromethyldichlorobenzene:* $C_6H_3Cl_2.CHCl_2$.—This substance is produced by the action of chlorine on boiling (2–0) dichlorotoluene. It is a liquid which boils constantly at 257° (494°·6 F.). It is slowly oxidized by chromic acid solution and converted into ordinary dichlorobenzoic acid; when heated with water at 220° (428° F.) it furnishes dichlorobenzoic aldehyde, $C_6H_3Cl_2.COH$.

(1–3) *Tetrachlorotoluene. Trichloromethylchlorobenzene:* $C_6H_4Cl.CCl_3$.—This derivative has been produced by the action of chlorine in presence of iodine on (0–3) trichlorotoluene, but would doubtless be more readily formed by passing chlorine into boiling (1–0) chlorotoluene. It boils at 245° (473° F.), and when heated with water to 200° (392° F.) it is completely converted into hydrochloric acid and *para*chlorobenzoic acid. An isomeric body which furnishes *ortho*chlorobenzoic acid when heated with water, is formed by the action of phosphoric pentachloride on salicylic acid (Kolbe and Lautemann, *Ann. Chem. Pharm.*, cxv. 195); it is a crystalline solid, which melts at 30° (86° F.) and boils at 260° (500° F.). A third isomeride, furnishing *meta*chlorobenzoic acid when heated with water, is obtained by the action of phosphoric pentachloride on sulphobenzoic chloride, $C_6H_4\left\{\begin{matrix}SO_2Cl\\COCl\end{matrix}\right.$; it is a liquid which boils at 235° (455° F.).

(1333) PENTACHLOROTOLUENES.—In order to effect the displacement of the five atoms of hydrogen in the C_6H_5 group in toluene it is necessary to employ antimonic pentachloride.

(5–0) *Pentachlorotoluene*, or *Methylpentachlorobenzene*, $C_6Cl_5.CH_3$, boils without decomposition at 301° (573°·8 F.) and melts at 218° (424°·4 F.). It is only slightly soluble in the ordinary solvents, but is easily soluble in hot benzene, from which it crystallizes in long slender needles. It is not acted on by boiling concentrated nitric acid.

(4–1) *Pentachlorotoluene. Chloromethyltetrachlorobenzene:* $C_6HCl_4.CH_2Cl$.—This compound is formed by passing chlorine into boiling (4–0) tetrachlorotoluene. It is a liquid which boils almost without decomposition at 296° (564°·8 F.). With potassic acetate it furnishes the compound $C_6HCl_4.CH_2(C_2H_3O_2)$.

(3–2) *Pentachlorotoluene. Dichloromethyltrichlorobenzene:* $C_6H_2Cl_3.CHCl_2$, is formed by treating boiling dichlorotoluene with chlorine. It is a liquid which boils almost undecomposed at about 280° (536° F.), and solidifies below 0° (32° F.) to a mass of needles. It is converted by heating with water at 250° (482° F.) into trichlorobenzoic aldehyde, $C_6H_2Cl_3.COH$.

(2–3) *Pentachlorotoluene* or *trichloromethyldichlorobenzene*, $C_6H_3Cl_2.CCl_3$, is produced when chlorine is passed into boiling (2–0) dichlorotoluene until no further increase of weight takes place. It is a liquid which boils at 273° (523°·4 F.). When heated with water at 200° (392° F.) it yields dichlorobenzoic acid. Chlorine alone is entirely without action upon it, even at its boiling point.

(1334) HEXACHLOROTOLUENES.—The three modifications represented by the following formulæ are known:

$$C_6Cl_5.CH_2Cl \; ; \; C_6HCl_4.CHCl_2 \; ; \; C_6H_2Cl_3.CCl_3.$$

(5–1) *Hexachlorotoluene. Chloromethylpentachlorobenzene:* $C_6Cl_5.CH_2Cl$.—It is difficult to obtain this compound by the action of chlorine on boiling (5–0) pentachlorotoluene on account of the high boiling point of the latter, and it is therefore more readily prepared by passing chlorine into benzylic chloride mixed with iodine until no further absorption takes place. The product is a mixture of (3–1) tetrachlorotoluene and (4–1) pentachlorotoluene; it is washed with sodic hydrate solution, dried, and distilled: and as iodine is liberated on distillation, the washing, &c., is repeated *until the whole of the iodine is removed*. The chloride is then mixed with one-tenth of its weight of antimonious chloride, $SbCl_3$, and chlorine passed into the gently-warmed mixture until no further absorption occurs. If the whole of the iodine be not removed, only black resinous products are obtained, which decompose on distillation, and this is also the case in the preparation of (4–0) tetrachlorotoluene and (5–0) pentachlorotoluene. It crystallizes from a mixture of benzene and alcohol in fine needles, which melt at 103° (217°·4 F.). It boils without being decomposed at 325°–327° (617°–620°·6 F.). By heating to 200° (392° F.) with potassic acetate and alcohol it is converted into the compound $C_6Cl_5.CH_2(C_2H_3O_2)$.

(4–2) *Hexachlorotoluene. Dichloromethyltetrachlorobenzene:* $C_6HCl_4.CHCl_2$.—To prepare this compound chlorine is passed into boiling (4–0) tetrachlorotoluene as long as absorption takes place, and the mixture of (4–2) and (4–3) chlorotoluenes separated by fractional distillation. It is a liquid, and boils at 305° (581° F.). When heated with water to 250° (482° F.) it furnishes tetrachlorobenzoic aldehyde, $C_6HCl_4.COH$. In its preparation from tetrachlorotoluene a certain quantity of pentachlorobenzene is produced:

$$C_6HCl_4.CH_3 + 4Cl_2 = C_6HCl_5 + CCl_4 + 3HCl.$$

(3–3) *Hexachlorotoluene. Trichloromethyltrichlorobenzene:* $C_6H_2Cl_3.CCl_3$.—This body is formed by the action of chlorine on boiling (3–0) trichlorotoluene. It is purified by fractional distillation and crystallization from alcohol. It forms long white needles, which melt at 82° (179°·6 F.), and it boils at 308° (586°·4 F.). By the action of water at 250° (482° F.) it is converted into trichlorobenzoic acid. $C_6H_2Cl_3.COOH$. In the preparation of this compound a quantity of tetrachlorobenzene (melting at 139° C.) is always produced:

$$C_6H_2Cl_3.CCl_3 + Cl_2 = C_6H_2Cl_4 + CCl_4.$$

(1335) HEPTACHLOROTOLUENES.—The modification (5–2) or *dichloromethylpentachlorobenzene*, $C_6Cl_5.CHCl_2$, is prepared from (0–2) dichlorotoluene, which is treated with chlorine in presence of iodine as long as an increase of weight takes place; the product is then freed from iodine, digested with three or four times its weight of antimonic pentachloride and distilled. The crude product consists of (5–2) and a small quantity of (4–3) heptachlorotoluene, together with a substance insoluble in alcohol. The 5–2 modification is obtained pure by crystallization from alcohol after heating with water to 300° (572° F.), by which it is not affected, but which converts the (4–3) modification into tetrachlorobenzoic acid. It crystallizes in long pointed plates, melting at 109° (228°·2 F.), and boils undecomposed at 334°·2 (633°·2 F.).

(4–3) *Heptachlorotoluene. Trichloromethyltetrachlorobenzene:* $C_6HCl_4.CCl_3$, is most readily obtained by the action of chlorine on boiling (4–0) tetrachlorotoluene. It crystallizes in short fine needles or white plates, melting at 104° (219°·2 F.), and boils at 316° (600°·8 F.). It is not altered by distillation with antimonic pentachloride.

All attempts to prepare an octochlorotoluene, $C_6Cl_5.CCl_3$, were unsuccessful. Thus on distilling (3–3) and (5–1) hexachlorotoluene with antimonic pentachloride, the product consisted of hexachlorobenzene, C_6Cl_6, and the same compound was obtained on heating (4–3) and (5–2) heptachlorotoluene with the chloride in sealed tubes to 280° (536° F.).

In the following table a list of the chloro-derivatives of toluene, together with their boiling points (° C.) and specific gravities are given. Unless otherwise stated the temperatures are uncorrected.

CHLORO-DERIVATIVES OF TOLUENE.

0–0 (Toluene).	0–1	0–2	0–3
B.P. 111° Sp. Gr. 0·882 at 0°	B.P. 176° Sp. Gr. 1·117 at 0°	B.P. 205° Sp. Gr. 1·255 at 14°	B.P. 214° Sp. Gr. 1·380 at 14°
1–0	1–1	1–2	1–3
(Para) B.P. 160°·5* (Meta) B.P. 156°	B.P. 214° Sp. Gr. 1·297 at 22°	B.P. 234°	(Para) B.P. 245° Sp. Gr. 1·495 at 14° (Meta) B.P. 235° (Ortho) B.P. 260° M.P. 30°
2–0	2–1	2–2	2–3
B.P. 196° Sp. Gr. 1·234 at 21°	B.P. 241°	B.P. 257° Sp. Gr. 1·518 at 22°	B.P. 273° † Sp. Gr. 1·587 at 21°
3–0	3–1	3–2	3–3
B.P. 235° M.P. 76°	B.P. 273° Sp. Gr. 1·547 at 23°	B.P. 281° Sp. Gr. 1·607 at 22°	B.P. 308° M.P. 82°
4–0	4–1	4–2	4–3
B.P. 271° M.P. 91°	B.P. 296° Sp. Gr. 1·634 at 25°	B.P. 306° Sp. Gr. 1·704 at 25°	B.P. 316° M.P. 104°
5–0	5–1	5–2	5–3
B.P. 301° M.P. 218°	B.P. 326° M.P. 103°	B.P. 334° M.P. 109°	

(1336) CHLORO-DERIVATIVES OF THE HOMOLOGUES OF TOLUENE.—*Chloroxylenes.*—When chlorine is allowed to act upon boiling coal tar xylene a monochloro-derivative, $C_6H_4\left\{\begin{matrix}CH_3\\CH_2Cl,\end{matrix}\right.$ is obtained, which in all respects resembles benzylic chloride; it is a liquid which boils constantly at 193° (379°·4 F.), and exerts a most irritating action upon the eyes. By the further action of chlorine, the dichloro-derivative, $C_6H_4\left\{\begin{matrix}CH_2Cl\\CH_2Cl,\end{matrix}\right.$ is produced. This crystallizes in rhombic plates melting at 100° (212° F.), and boils at 240°–245° (464°–473° F.), but at the same time undergoes decomposition. It readily exchanges both atoms of chlorine for other radicles. On oxidation it furnishes terephthalic acid, $C_6H_4(COOH)_2$, and is, in fact, a paraxylene derivative.

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* This is the B.P. of pure parachlorotoluene; but the product from toluene also contains orthochlorotoluene, and the 1–1, 1–2, and 1–3 derivatives prepared from it are doubtless, therefore, mixtures of isomeric bodies, although they consist chiefly of the para-derivative.

† Aronheim and Dietrich have obtained a liquid isomeride from toluene boiling at about 280°.

When chlorine acts upon xylene in presence of iodine, however, chloroxylenes are obtained which do not exhibit the slightest tendency to exchange chlorine for other radicles. *Monochloroxylene*, $C_6H_3Cl(CH_3)_2$, boils at 184° (363°·2 F.); on oxidation with chromic acid mixture it is slowly converted into a *chlorotoluic acid*, $C_6H_3Cl(CH_3).COOH$, which melts at 203° (397°·4 F.). *Dichloroxylene* is crystalline at a low temperature, and boils at 222° (431°·6 F.); when oxidized it furnishes dichlorotoluic acid melting at 160° (320° F.). *Trichloroxylene* crystallizes from alcohol in white needles melting at 150° (302° F.), and it boils at 255° (491° F.) without undergoing the slightest decomposition. It is not in the least attacked either by nitric acid, or by chromic acid mixture, and it is noteworthy that whereas both methyl groups in xylene are readily oxidized, only one of them in chloro- and dichloroxylene is converted into COOH, and that in trichloroxylene neither is affected by oxidizing agents. It has not been determined from which of the xylenes these chloroxylenes are derived. By the continued action of chlorine on xylene, first in presence of iodine, and afterwards in presence of antimonic chloride, hexachlorobenzene is produced. (Vollrath, *Ann. Ch. Pharm.*, cxliv. 261; Lauth and Grimaux, *ibid.* cxlv. 115; clv. 338; Biedermann, *Deut. chem. Ges. Ber.*, vi. 702).

Chloromesitylenes.—Chlorine acts upon well cooled mesitylene with great energy, and the tendency to form trichloromesitylene is so pronounced that this compound is always obtained together with the lower derivatives, even when only sufficient chlorine is employed to convert the amount of hydrocarbon taken into the monochloro-derivative. To separate these substances, the crude product, after it has been washed with sodic hydrate solution, is dissolved in boiling alcohol; almost the whole of the trichloromesitylene separates on cooling, and is purified by several recrystallizations from alcohol. The mono- and dichloromesitylene are precipitated from the mother liquor by water, and separated by fractional distillation.

Monochloromesitylene, $C_6H_2Cl(CH_3)_3$, is a colourless liquid which boils at 204°—206° (399°·2—402°·8 F.); it does not solidify at −20°(−4° F.). Fuming nitric acid converts its almost instantly into a mixture of nitro- and dinitrochloromesitylene. On oxidation by dilute nitric acid it is converted into chloromesitylenic acid, $C_6H_2Cl(CH_3)_2.COOH$, but when it is oxidized with chromic acid mixture only acetic acid is obtained.

Dichloromesitylene, $C_6HCl_2(CH_3)_3$, crystallizes from alcohol in colourless glistening prisms which melt at 59° (138°·2 F.); it boils at 244° (471°·2 F.). Chromic acid mixture is almost without action upon it.

Trichloromesitylene, $C_6Cl_3(CH_3)_3$, crystallizes from alcohol in long slender needles, which melt at 205° (401° F.). It is not affected even by long boiling with moderately concentrated nitric acid (Fittig and Hoogewerff, *ibid.* cl. 323).

(1337) BROMO-DERIVATIVES OF TOLUENE.—The action of bromine on toluene varies according to the temperature: thus with boiling toluene (0—1) bromotoluene or benzylic bromide, $C_6H_5.CH_2Br$, is produced. This compound closely resembles benzylic chloride, readily exchanging bromine for other radicles; it boils at about 202° (395°·6 F.), and at 22° (71°·6 F.) has the sp. gr. 1·438. Its vapour exercises a most irritating effect upon the eyes. According to Körner (*Giornale di Scienze naturali ed economiche, Palermo*, 1869, v. 244), when bromine and toluene, both cooled to 0° (32° F.), are carefully mixed, a considerable quantity of benzylic bromide is also formed—although under these circumstances the reaction only takes place very slowly; after 48 hours, however, the product is found to contain from 200 to 330 grms. of benzylic bromide for every 1000 of (1—0) bromotoluenes. At the temperature of 9°—12° (48°·2—53°·6 F.), on the contrary, bromine readily acts upon toluene, and if the former be slowly added and the mixture allowed to stand 24 hours it contains only from 9 to 26 grms. of benzylic bromide for every 1000 grms. of (1—0) bromotoluenes.

A mixture of (1—0) bromotoluenes is thus formed, consisting chiefly of parabromotoluene (CH_3 : Br = 1 : 4), but always containing a considerable amount of orthobromotoluene (1 : 2); according to Körner, the third isomeride is also present in small quantity. The pure (1—0) bromotoluenes may be obtained by Griess's method from the pure amidotoluenes or toluidines. The (1—0) bromotoluenes are extremely inert substances, and their vapours have no irritating action upon the eyes; parabromotoluene is crystalline, and melts at 28°·5 (83°·3 F.), whilst the isomerides are liquid, and of lower specific gravity than (0—1) bromotoluene, viz., about 1·40 at 20° (68° F.). The boiling points (° C.) of these compounds, according to Körner, are as follows:

Parabromotoluene (1 : 4)	...	184°·6
Metabromotoluene (1 : 3)	...	184°·5
Orthobromotoluene (1 : 2)	...	182°

Dibromotoluenes.—Although toluene is readily converted into (1—0) bromotoluenes, the displacement of a second atom of hydrogen by bromine takes place but very slowly: even after many days contact only a very small quantity of a crystalline (2—0) dibromotoluene being obtained (Fittig). By adding iodine to the mixture of bromotoluenes and bromine and exposing it to sunlight for several days, however, a liquid (2—0) dibromotoluene boiling at 239°—241° (462°·2—465°·8 F.) is readily obtained (Jannasch, *Ann. Chem. Pharm.*, clxxvi. 286); the nature of this product has not yet been determined, but in all probability it is a mixture of isomeric (2—0) dibromotoluenes consisting chiefly of the modification (CH_3 : Br : Br = 1 : 3 : 4). Wroblevsky (*ibid.* clxviii. 147) has prepared a number of isomeric dibromotoluenes by Griess's reaction from the bromamidotoluenes or bromotoluidines, but their constitution in all cases has not been satisfactorily determined; their properties are given in the following table:

DESCRIPTION.	Constitution CH_3 : Br : Br.	M.P. °Cent.	B.P. °Cent.	M.P. of Nitro-derivative.
From toluene (Fittig)	1 : 2 : 4 (?)	107—108	245	—
From dibromoparatoluidine	1 : 3 : 5	60	241	124
From dibromorthotoluidine and orthobromometatoluidine.	1 : 2 : 3 (?)	42·5	239	59
From metabromorthotoluidine and by brominating metabromotoluene.	1 : 2 : 5 (?)	liquid	238—239	86—87
From dibromometatoluidine	1 : 2 : 6 (?)	,,	246	79
From metabromoparatoluidine	1 : 3 : 4	,,	237	86—87*

(0—2) Dibromotoluene, $C_6H_5.CHBr_2$, prepared by the action of phosphoric pentabromide on benzoic aldehyde, is a liquid which is decomposed on distillation.

Tribomotoluenes.—Wroblevsky has obtained two (3—0) tribromotoluenes: the modification CH_3 : Br. : Br. : Br. = 1 : 3 : 4 : 5 by Griess's reaction from dibromoparatoluidine, and the modification 1 : 2 : 4 : 6 (?) from tribrommetatoluidine. The former is a colourless liquid which boils at 260° (500° F.); the latter crystallizes in long needles which melt at 70° (158° F.), and it boils at 290° (554° F.).

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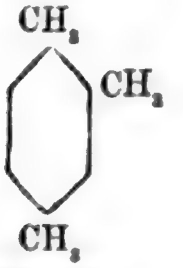
* The dibromotoluidine formed on reducing this compound melts at 95°, that derived from the isomeride from the dibromotoluene from metabromorthotoluidine melting at 83°.

(1338) **Bromoxylenes.**—When bromine is added to well cooled paraxylene, a *paradimethylbromobenzene*, $C_6H_3Br(CH_3)_2$, is produced, which may be obtained in glistening colourless plates melting at 10° (50° F.), and which boils at 200° (392° F.) (Jannasch). By the action of an excess of bromine a *paradimethyldibromobenzene*, $C_6H_2Br_2(CH_3)_2$, is produced; this crystallizes in colourless laminæ which melt at 72° (161°·6 F.). It boils at 256° (492°·8 F.). By the action of bromine on boiling paraxylene an isomeric body, $C_6H_4(CH_2Br)_2$, is obtained which melts at 145°—147° (293°—296° F.); the bromine in this compound is readily displaced by other radicles.

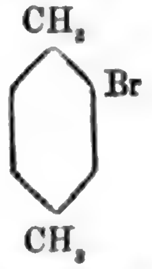
Metadimethylbromobenzene or *bromometaxylene*, $C_6H_3Br(CH_3)_2$, is liquid, and boils at 205° (401° F.); *metadimethyldibromobenzene*, $C_6H_2Br_2(CH_3)_2$, resembles dibromoparaxylene in all respects. Metaxylene also furnishes a *tetrabromo*-derivative, $C_6Br_4(CH_3)_2$, which melts at 241° (465°·8 F.); it crystallizes from alcohol, in which it is difficultly soluble, in long slender needles.

Bromo-derivatives of orthoxylene have not been prepared in a pure state.

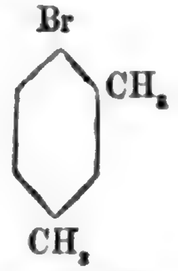
Inasmuch as the monobromo-derivative of each of the three xylenes is convertible into pseudocumene (p. 288), it necessarily follows that bromine always takes up such a position as to form a derivative of the 1 : 2 : 4 series, and that the constitution of the bromoxylenes is that represented by the following figures:



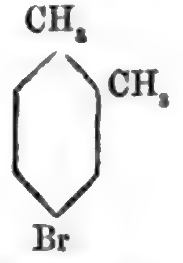
Pseudocumene.



Bromoparaxylene.



Bromometaxylene.



Bromorthoxylene.

(1339) **Bromethylbenzene.**—By the action of bromine on well cooled ethylbenzene, a liquid *ethylbromobenzene*, $C_6H_4Br.C_2H_5$, boiling at 199° (390°·2 F.), is obtained; this is doubtless a mixture of isomeric bodies, but consists chiefly of paraethylbromobenzene ($C_2H_5 : Br = 1 : 4$) as it furnishes parabromobenzoic acid on oxidation. When the hydrocarbon is heated to about 140° (284° F.), however, the compounds $C_6H_5.CHBr.CH_3$ and $C_6H_5.CHBr.CH_2Br$, are produced; the former is a liquid, and the latter a crystalline solid melting at 68° (154°·4 F.); both are very unstable substances, and readily enter into reactions of double decomposition, &c. (Thorpe, *Proc. Roy. Soc.*, xviii. 123; Radziszweski, *Deut. chem. Ges. Ber.*, vi. 492).

(1340) **Bromotrimethylbenzenes.**—Bromomesitylene is a colourless liquid, which becomes solid when cooled below 0° (32° F.), and boils at 225° (437° F.). The isomeric bromopseudocumene forms crystalline laminæ which melt at 73° (163°·4 F.) Tribromomesitylene and tribromopseudocumene, however, are both crystalline and melt at 224° (435°·2 F.).

The alteration in properties induced by the introduction into benzene of one or more methyl groups in place of hydrogen comes out very strongly in the formation of the bromo-derivatives. Thus the conversion of benzene into bromobenzene takes place very slowly, but toluene is readily converted into bromotoluene; the formation of a dibromotoluene, however, takes place with much greater difficulty than that of dibromobenzene. The xylenes are rapidly transformed into dibromo-derivatives by the action of a slight excess of bromine, and the trimethylbenzenes furnish tribromo-derivatives with such readiness that it is necessary to add the bromine with the greatest caution in order to obtain mono-derivatives.

(1341) BROMO-DERIVATIVES OF OTHER HOMOLOGUES OF BENZENE.—Very few of the bromo-derivatives of the remaining hydrocarbons of the benzene series have been carefully examined, although a considerable number of them have been prepared; several interesting subjects for inquiry, therefore, still present themselves in this direction. For instance, we do not know what is the action of chlorine and bromine on hydrocarbons containing two (or more) *different* side chains, *i.e.* in which of the side chains the hydrogen will first be displaced—whether in the more or the less complex group—supposing the action to take place upon the heated hydrocarbon. Is cymene, for instance, converted by the action of chlorine into $C_6H_4\left\{\begin{matrix}C_3H_6Cl\\CH_3\end{matrix}\right.$, or into $C_6H_4\left\{\begin{matrix}C_3H_7\\CH_2Cl\end{matrix}\right.$?

(1342) IODO-DERIVATIVES OF THE HOMOLOGUES OF BENZENE.—So few of these have been obtained, and so little is known about them, that at present they do not possess any great interest. All that are known have been prepared from the corresponding amido-derivatives by Griess's method.

Nitro-derivatives of Benzene and its Homologues.

(1343) *Preparation and Properties.*—The nitro-derivatives of the members of the benzene series are readily obtained from the corresponding hydrocarbons by the action of concentrated nitric acid, or a mixture of concentrated nitric and sulphuric acids. In this reaction it is always the hydrogen in the C_6 nucleus which is displaced, but up to the present time it has not been found possible to introduce more than three monad NO_2 groups in place of the corresponding number of hydrogen atoms.

With few exceptions, the nitro-derivatives are crystalline bodies, almost insoluble in water, but readily dissolved by alcohol, benzene, and many other solvents. Their behaviour when treated with reducing agents, such as an alcoholic solution of ammonic sulphide, tin and hydrochloric acid, &c., is very characteristic, as they are converted into the corresponding *amido*-derivatives, the NO_2 group being changed into the NH_2 group. In the case of the di- and tri-nitro-derivatives, it is possible to reduce the NO_2 groups one by one. Thus by the action of ammonic sulphide on the dinitrobenzenes *amidonitrobenzenes* or *nitranilines* are obtained:

$$\underset{\text{Dinitrobenzene.}}{C_6H_4(NO_2)_2} + 3SH_2 = \underset{\text{Amidonitrobenzene.}}{C_6H_4(NO_2)(NH_2)} + 2OH_2 + 3S;$$

which, by further treatment with a more powerful reducing agent, such as tin and hydrochloric acid, are converted into *diamidobenzenes*:

$$C_6H_4(NO_2)(NH_2) + 3H_2 = C_6H_4(NH_2)_2 + 2OH_2.$$

Sometimes, however, the NO_2 group is not only reduced to NH_2, but the NH_2 group is removed in the form of ammonia and displaced by hydrogen. Trinitromesitylene, for example, is converted on treatment with tin and hydrochloric acid into diamidomesitylene, the triamidomesitylene which, doubtless, is first formed, being further acted upon:

$$\underset{\text{Trinitromesitylene.}}{C_6(CH_3)_3(NO_2)_3} + 9H_2 = \underset{\text{Triamidomesitylene.}}{C_6(CH_3)_3(NH_2)_3} + 6OH_2;$$

$$\underset{\text{Triamidomesitylene.}}{C_6(CH_3)_3(NH_2)_3} + H_2 = \underset{\text{Diamidomesitylene.}}{C_6H(CH_3)_3(NH_2)_2} + NH_3.$$

NITRO-DERIVATIVES OF BENZENE.

(1344) **Nitrobenzene**: $C_6H_5.NO_2$.—This compound is readily prepared by adding benzene to fuming nitric acid placed in a vessel surrounded with water, the mixture being allowed, however, to become somewhat warm. The product is washed, dried with calcic chloride, and distilled. Nitrobenzene is a pale yellow liquid, having an odour resembling that of bitter-almond oil, on which account it is much used by perfumers under the name of '*Essence de Mirbane.*' It boils at 212°—213° (413°·6—415°·4 F.). When cooled below 3° (37°·4 F.) it crystallizes in prisms. Nitrobenzene is a remarkably stable substance, not being attacked by chlorine or bromine even at its boiling-point: in presence of iodine or antimonic pentachloride, however, chlorine acts upon it, forming metachloronitrobenzene and nitroparadichlorobenzene. Bromine also, when heated with it to 250° (482° F.) gives rise to bromobenzenes, the oxygen of the nitro-group appearing partly in the form of water, partly in the form of carbonic anhydride, whilst the nitrogen is evolved as such.

Fuming sulphuric acid dissolves nitrobenzene, forming a mixture of isomeric nitrobenzenesulphonic acids, $C_6H_4(NO_2)(HSO_3)$.

Nitrobenzene is scarcely affected by a boiling aqueous solution of potassic hydrate, but by the action of an alcoholic solution it is converted into *azoxybenzene*, $(C_6H_5N)_2O$, and *azobenzene*, $(C_6H_5)_2N_2$. Nitrobenzene is converted by most reducing agents into *aniline* or *amidobenzene* (phenylamine):

$$\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + 3H_2 = \underset{\text{Amidobenzene.}}{C_6H_5.NH_2} + 2OH_2.$$

When it is reduced by the action of ammonic sulphite, however, the ammonic salt of *phenylsulphamic acid* is produced,

$$C_6H_5.NH(SO_3NH_4).$$

(1345) **Dinitrobenzenes**: $C_6H_4(NO_2)_2$.—When nitrobenzene is gradually introduced into a mixture of equal volumes of the strongest nitric acid and fuming sulphuric acid until it ceases to be dissolved, and the mixture is then gently heated for some hours, until, on testing a portion, it is found that the oil which separates on the addition of water solidifies entirely on cooling, it is converted into dinitrobenzenes. The product, however, contains *three* isomeric compounds, of which the metadinitrobenzene ($NO_2 : NO_2 = 1 : 3$) is present in by far the largest quantity. These isomerides may be separated by systematic crystallization from alcohol (*Chem. Soc. Journ.*, xxix. 207).

Paradinitrobenzene (1 : 4) crystallizes from alcohol in nearly colourless flat needles melting at 171°—172° (339°·8—341°·6 F.); it is almost insoluble in water, moderately soluble in ether, benzene, or chloroform, and slightly soluble in cold alcohol.

Metadinitrobenzene (1 : 3) crystallizes in long glistening almost colourless needles, and melts at 89°·8 (193°·8 F.). It is extremely soluble in boiling alcohol, but only slightly soluble in cold alcohol.

Orthodinitrobenzene (1 : 2) crystallizes from dilute alcohol in almost colourless needles, resembling sublimed benzoic acid, and from absolute alcohol in large, striated, pale golden-yellow prisms or large transparent tables. It melts at 117°·9 (244°·2 F.), but a mixture of equal parts of meta- and orthodinitrobenzene melts constantly at 64°—65° (147°·2—149 F.); it is considerably less soluble in boiling alcohol than the meta- compound.

(1346) **Nitrotoluenes**.—By the action of nitric acid on toluene, a mixture of *para-* and *orthonitrotoluene* in variable proportions is produced: the more violent the reaction—that is to say, the stronger the acid, and the higher the temperature at which it takes place,—the greater is the proportion of paranitrotoluene; the amount of paranitrotoluene produced, however, never exceeds 64·8 per cent., and is never less than 33·3 per cent. of the total product (Rosenstiehl, *Ann. Chem. Phys.* [4], xxvii. 433). Beilstein and Kuhlberg affirm that the two nitrotoluenes may be separated by repeated fractional distillation, but Rosenstiehl, who has examined the action of nitric acid on toluene in a most careful and exhaustive manner, and whose memoir on the subject deserves attentive study, states that it is impossible entirely to separate them in this manner; in fact, although the pure para-derivative may be isolated from the mixture, pure orthonitrotoluene can only be obtained indirectly from toluene. Pure paranitrotoluene is readily prepared from the crude product by cooling it by means of a good refrigerating mixture; the crystals which separate are removed and purified by crystallization from alcohol. Pure orthonitrotoluene may be obtained by Griess's method from the amidonitrotoluene, $C_6H_3.NH_2.NO_2.CH_3$, prepared by reducing orthoparadinitrotoluene with ammonic sulphide (Beilstein and Kuhlberg, *Ann. Chem. Pharm.*, clv. 1).

A third modification, *metanitrotoluene*, is formed on nitrating acetoparamidotoluene or paracetoluid, $C_6H_4.CH_3.NH(C_2H_3O)$, and displacing, by Griess's method, the NH_2 group in the nitroparamidotoluene obtained from this compound, by hydrogen. The three isomeric nitrotoluenes have the following properties:

	Melting-point.	Boiling-point.	Sp. gr.
Paranitrotoluene	54° (Cent.)	236° (uncor.)	—
Metanitrotoluene	liquid	231° „	1·168 at 22°.
Orthonitrotoluene	liquid	223° „	1·163 at 23°·5.

By the action of chromic acid mixture, para- and metanitrotoluene are readily oxidized to para- and metanitrobenzoic acids, $C_6H_4.NO_2.COOH$, whilst orthonitrotoluene is completely decomposed under these circumstances.

Dinitrotoluenes.—By the action of the strongest nitric acid, or a mixture of nitric and sulphuric acids, on paranitrotoluene, *orthoparadinitrotoluene* ($CH_3 : NO_2 : NO_2 = 1 : 2 : 4$) is produced; it crystallizes in almost colourless needles, which melt at about 70° (158° F.). The same body is obtained, together with a liquid isomeride, which is probably *diorthodinitrotoluene* ($CH_3 : NO_2 : NO_2 = 1 : 2 : 6$), by nitrating orthonitrotoluene (Rosenstiehl, *loc. cit.*; Cunerth, *Ann. Chem. Pharm.*, clxxii. 221). A third dinitrotoluene is produced by agitating metanitrotoluene with the strongest nitric acid for some time; it forms long colourless needles, which melt at 60° (140° F.) (Beilstein and Kuhlberg, *loc. cit.*).

Trinitrotoluenes.—By heating orthoparanitrotoluene with a mixture of fuming sulphuric and nitric acids it is gradually converted into a trinitrotoluene, which melts at 80°·5 (176°·9 F.); the same compound is obtained on similarly treating the mixture of nitrotoluenes formed by nitrating toluene. As this compound on reduction furnishes a dinitroamidotoluene identical with that formed from the dinitroparacetoluid, produced by nitrating paracetoluid, there can be but little doubt that the NO_2 groups are in the positions 2 : 4 : 6 relatively to the CH_3 group.

An isomeric trinitrotoluene is produced by nitrating metanitrotoluene (Beilstein and Kuhlberg, *loc. cit.* and clviii. 341; Tiemann, *Deut. chem. Ges. Ber.*, iii. 217; Mills, *Phil. Mag.*, 1875).

(1347) NITROXYLENES.—As the xylenes are converted into dinitro-derivatives with the greatest readiness, the preparation of the mononitroxylenes is a matter of some difficulty. *Nitroparadimethylbenzene*, $C_6H_3(NO_2)(CH_3)_2$, is obtained by carefully adding the calculated amount of nitric acid to well cooled paraxylene; it is a colourless oil which boils at 234°—237° (453°·2—458°·6 F.) (Jannasch, *Ann. Chem. Pharm.*, clxxvi. 55). By the action of a slight excess of fuming nitric acid on paraxylene, a mixture of two isomeric *dinitro*-derivatives, in about equal quantities, is produced, one of which melts at 93° (199°·4 F.), and the other at 125° (257° F.); they may be separated by crystallization from alcohol, the former being more soluble than the latter (Jannasch, *ibid.* clxxi. 81). By the action of a mixture of concentrated sulphuric and fuming nitric acids, paraxylene is converted into *trinitroparaxylene*, even in the cold if allowed to stand for some time; this is much more soluble in hot alcohol than the isomeric metaxylene derivative, and crystallizes in larger colourless needles, which melt at 137° (278°·6 F.) (Fittig, Ahrens and Mattheides, *ibid.* cxlvii. 23).

Nitrometaxylene, prepared by Griess's method, from the amidonitrometaxylene from dinitrometaxylene, melts at 2° (35°·6 F.), and boils at 237°—239° (458°·6—462°·2 F.). By gently warming the solution of metaxylene in fuming nitric acid, it is entirely converted into *dinitrometaxylene*, which melts at the same temperature as the isomeric paraxylene derivative; it crystallizes in large colourless flattened needles; whereas the dinitroparaxylene, which melts at 93°, forms large well developed monoclinic prisms. By gently warming with a mixture of sulphuric and nitric acids metaxylene is rapidly converted into the *trinitro*-derivative, which melts at 176° (348°·8 F.), and crystallizes in thin colourless flattened needles (*loc. cit.*).

The nitro derivatives of orthoxylene have not been examined; even after prolonged heating with nitric acid it only furnishes liquid products.

(1348) NITROTRIMETHYLBENZENES.—Pseudocumene is readily converted into the mononitro-derivative by the action of cold fuming nitric acid. *Nitropseudocumene* crystallizes in long almost colourless needles, which melt at 71° (159°·8 F.); it may be dissolved in cold fuming nitric acid unchanged, whereas the isomeric nitromesitylene is so readily converted into the dinitro-derivative, that the latter is obtained almost as sole product on dropping mesitylene into cold fuming nitric acid. Pure dinitropseudocumene has not been obtained. Pseudocumene readily furnishes the trinitro-derivative when added to a cold mixture of 2 vols. concentrated sulphuric acid with 1 vol. fuming nitric acid. *Trinitropseudocumene* crystallizes in colourless prisms, which melts at 185° (365° F.) (Fittig and Laubinger, *Ann. Chem. Pharm.*, cli. 259).

Nitromesitylene, obtained by the action of ordinary nitric acid (sp. gr. 1·38) on mesitylene, crystallizes in well developed pale yellow prisms, which melt at 41° (105°·8 F.) (Fittig and Storer, *ibid.*, cxlvii. 1; Biedermann and Ledoux, *Deut. chem. Ges. Ber.*, viii. 57).

Dinitromesitylene forms fine colourless, glistening rhombic crystals, which melt at 86° (186°·8 F.); it is one of the most characteristic derivatives of mesitylene. Mesitylene is converted in a few minutes into *trinitromesitylene* by the action of a cold mixture of 1 vol. of fuming nitric with 2 vols. concentrated sulphuric acid; it crystallizes in colourless needles, which melt at 232° (449°·6 F.), and are very difficultly soluble in hot alcohol: trinitropseudocumene, on the contrary, dissolves readily (Fittig, *Ann. Chem. Pharm.*, cxli. 132).

It is noteworthy that, to convert benzene into nitrobenzene, it is necessary to employ very strong nitric acid, and even then the action is of a very mild character, whilst dinitrobenzene is only formed after heating with a mixture of the strongest nitric and sulphuric acids. Toluene is far more readily converted into nitrotoluene, and furnishes dinitrotoluene with no great difficulty; it may even be converted into *tri*nitrotoluene by prolonged warming with nitric and sulphuric acids. The dimethylbenzenes readily furnish dinitro-derivatives; and, lastly, the trimethylbenzenes are so readily converted into trinitro-derivatives that special precautions are required in order to prevent their formation when lower derivatives are being prepared.

Very little is known of the nitro-derivatives of the remaining hydrocarbons of the benzene series. By the action of nitric acid on ethylbenzene, Beilstein and Kuhlberg (*ibid.* clvi. 206) have obtained a mixture of isomeric *ethylnitrobenzenes*, $C_6H_4.NO_2.C_2H_5$, corresponding to the mixture of isomeric nitrotoluenes formed on nitrating toluene. Both are liquid and boil respectively at 245° (473° F.) and 227° (440°·6 F.); the former is converted into paranitrobenzoic acid on oxidation, but the latter does not furnish a corresponding acid.

Cymene also yields two mononitro-derivatives; the chief product is liquid, the isomeric compound, however, is crystalline, and melts at 125° (257° F.) (Fittica, *ibid.* clxxii. 313).

Cyano-Derivatives of Benzene and its Homologues.

(1349) CYANO-DERIVATIVES OF BENZENE. — *Cyanobenzene, Phenylic cyanide,* or *Benzonitrile:* $C_6H_5.CN$ or $C_6H_5.C{\equiv}N$.—This compound may be obtained

1. By distilling a mixture of the potassic or sodic salt of benzenesulphonic acid with potassic cyanide or ferrocyanide:

$$\underset{\text{Potassic benzenesulphonate.}}{C_6H_5.SO_3K} + KCN = \underset{\text{Cyanobenzene.}}{C_6H_5.CN} + SO_3K_2.$$

2. By distilling benzamide with phosphoric anhydride or pentasulphide:

$$\underset{\text{Benzamide.}}{C_6H_5.CO.NH_2} + P_2O_5 = \underset{\text{Cyanobenzene.}}{C_6H_5.CN} + 2HPO_3.$$

3. By digesting together potassic thiocyanate and benzoic acid, and afterwards distilling (Letts, *Deut. chem. Ges. Ber.*, v. 673). Probably benzamide is first produced and subsequently resolved into cyanobenzene and water under the influence of the potassic benzoate (Kekulé, *ibid.* vi. 112):

$$\underset{\text{Benzoic acid.}}{2C_6H_5.COOH} + \underset{\substack{\text{Potassic}\\\text{thiocyanate.}}}{KCNS} = \underset{\text{Benzamide.}}{C_6H_5.CO.NH_2} + \underset{\substack{\text{Carbonic}\\\text{oxysulphide.}}}{COS} + \underset{\substack{\text{Potassic}\\\text{benzoate.}}}{C_6H_5.COOK}.$$

4. Cyanobenzene is also formed by distilling the product of the action of benzoic chloride on argentic cyanate (Schützenberger):

$$\underset{\text{Benzoic chloride.}}{C_6H_5.COCl} + AgOCN = \underset{\text{Benzoic cyanate.}}{C_6H_5.COOCN} + AgCl;$$

$$\underset{\text{Benzoic cyanate.}}{C_6H_5.COOCN} = \underset{\text{Cyanobenzene.}}{C_6H_5.CN} + CO_2.$$

5. By distilling a mixture of oxalic acid and aniline (Hofmann).

6. By digesting phenylic isothiocyanate with finely divided metallic copper at its boiling point; the isothiocyanate, $C_6H_5.NCS$, is doubtless first converted into the isocyanide or isocyanobenzene, $C_6H_5.NC$, which then undergoes isomeric change and is transformed into cyanobenzene; this is rendered highly probable by the fact that when isocyanobenzene is heated alone in sealed tubes for 2—3 hours to 200°—220° (392°—428° F.) it undergoes this change (Weith, *ibid.* vi. 210).

Cyanobenzene is a colourless mobile liquid having an odour somewhat resembling that of bitter almonds; it boils at 191°

(375°·8 F.). When heated with water it is slowly converted into ammonic benzoate, but it is far more readily decomposed in presence of acids or alkalies; on boiling with an alcoholic solution of potassic hydrate it is rapidly converted into potassic benzoate. Cyanobenzene combines with the haloid acids, forming compounds such as $C_7H_5N,2HBr$ and C_7H_5N,HCl. By the action of fuming nitric acid it is converted into crystalline *metanitrocyanobenzene*, $C_6H_4.NO_2.CN$. When heated with bromine to 140°—150° (284°—302° F.) it furnishes a small quantity of a substance of the composition $C_7H_5NBr_2$ (? $C_7H_4BrN.HBr$); a crystalline body represented by the empirical formula C_7H_5NBr, the nature of which has not been determined; and a viscid substance (Engler).

Cyanobenzene is readily polymerized. Thus when it is gently heated with sodium it furnishes *cyaphenine*—a body of the same empirical composition as the original substance—together with sodic cyanide and another carbon compound (Hofmann). Cyaphenine is also formed by the action of benzoic chloride on potassic cyanate (Cloez); and from the compound C_7H_5NBr from cyanobenzene, which, when heated, splits up into cyaphenine, bromine, and cyanobenzene. Cyaphenine is only slightly soluble in alcohol or ether, but readily soluble in carbonic disulphide; it crystallizes in small needles which melt at 224° (435°·2 F.). It does not furnish ammonia when boiled with an alcoholic solution of potassic hydrate (Engler, *Ann. Chem. Pharm.*, cxlix. 310). It dissolves in sulphuric acid, being converted into a sulpho-acid; whilst fuming nitric acid transforms it into a crystalline mononitro-derivative.

Isocyanobenene, Phenylic isocyanide, or *Phenylcarbamine*: $C_6H_5.NC$ or $C_6H_5.N{\equiv}C$.—This compound is formed on distilling a mixture of chloroform, aniline, and an alcoholic solution of potassic hydrate (Hofmann, *ibid.* cxliv. 117):

$$\underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Aniline.}}{C_6H_5.NH_2} + 3KHO = \underset{\text{Isocyanobenzene.}}{C_6H_5.NC} + 3KCl + 3OH_2.$$

It is a mobile liquid, blue by reflected and green by transmitted light. It has a pungent, most unpleasant, aromatic odour like that of hydrocyanic acid, and its vapour produces an intensely bitter taste upon the tongue, and a suffocating sensation in the throat. It boils at about 160° (320° F.), but is at the same time partially decomposed. It is easily distinguished from the isomeric compound by the energy with which it enters into reaction with various bodies. Thus it unites very readily with metallic cyanides forming crystalline double cyanides, and when heated with sulphur combines with it to form phenylic isothiocyanate. $C_6H_5.NCS$ (Weith, *Deut. chem. Ges. Ber.*, vi. 210); benzonitrile, on the contrary, unites but slowly with metallic cyanides, and does not combine with sulphur. The isocyanide, moreover, is scarcely altered by alkaline solutions, although they readily decompose benzonitrile; and it is easily decomposed even by dilute acids and with great evolution of heat by concentrated acids, whereas benzonitrile is affected by acids only on heating. The reactions which take place are represented by the following equations:

$$\underset{\text{Isocyanobenzene.}}{C_6H_5.NC} + OH_2 = \underset{\text{Phenylformamide.}}{C_6H_5.NH(HCO)};$$

$$\underset{\text{Phenylformamide.}}{C_6H_5.NH(HCO)} + OH_2 = \underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\text{Formic acid.}}{HCOOH.}$$

$$\underset{\text{Isocyanobenzene.}}{CN.C_6H_5} + \underset{\text{Aniline.}}{NH_2.C_6H_5} = \underset{\text{Methenyl- diphenyl-diamine.}}{CH\left\{\begin{array}{l}NH.C_6H_5\\ N.C_6H_5.\end{array}\right.}$$

Paradicyanobenzene: $C_6H_4(CN)_2$, (CN : CN = 1 : 4), prepared by distilling a mixture of the potassic salt of benzeneparadisulphonic acid, $C_6H_4(SO_3H)_2$, and potassic cyanide, crystallizes in long thin needles, and melts at about 220° (428° F.); when decomposed by boiling with potassic hydrate solution it furnishes *terephthalic acid*, $C_6H_4(COOH)_2$.

Metadicyanobenzene (CN : CN = 1 : 3), similarly prepared from benzenemetadisulphonic acid, crystallizes in fine short needles; it melts at 160° (320° F.), and yields *isophthalic acid* (Barth and Senhofer, *Deut. chem. Ges. Ber.*, viii. 254; 1481).

(1350) CYANO-DERIVATIVES OF THE HOMOLOGUES OF BENZENE.—A number of cyano-derivatives have been obtained by distilling mixtures of potassic cyanide with the potassic salts of the sulpho-acids, derived from the homologues of benzene, but little is known of them; in all of these the cyanogen is present in the C_6 group. Cyano-derivatives have also been formed from the chloro-derivatives of the homologues of benzene containing chlorine in the side chain, by double decomposition with potassic cyanide: the compounds $C_6H_5.CH_2.CN$, $C_6H_4(CH_2.CN)_2$, $C_6H_5.C_2H_4.CN$, $C_6H_4\left\{\begin{array}{l}CH_3\\ CH_2.CN\end{array}\right.$ and $C_6H_4\left\{\begin{array}{l}C_3H_7\\ CH_2.CN\end{array}\right.$, have been thus prepared. With the exception of the dicyano-derivative of xylene, which is crystalline, they are all colourless liquids.

Nitro-haloid Derivatives of Benzene and its Homologues.

(1351) The various haloid derivatives of benzene and its homologues, formed by the displacement of one or more atoms of hydrogen in the C_6 group by halogens, are all more or less readily converted into nitro-haloid derivatives by the action of nitric acid.

The haloid derivatives containing the halogen in the side chain appear also to yield nitro-haloid derivatives on careful treatment with nitric acid, although but very few compounds of this class have been obtained. The formation of nitro-haloid derivatives from nitro-derivatives has been realized in but a very limited number of cases; in fact, the only compounds which have been prepared in this way are *metachloronitrobenzene*, $C_6H_4Cl.NO_2$, and *nitroparadichlorobenzene*, $C_6H_3Cl_2.NO_2$, formed by the action of chlorine on nitrobenzene in presence of iodine or antimonic pentachloride, and *ortho-* and *paranitro-* (o—1) *chlorotoluene*, $C_6H_4.NO_2.CH_2Cl$, obtained by the action of chlorine on heated ortho- and paranitrotoluene (Wachendorff, *Deut. chem. Ges. Ber.*, viii. 1101). A considerable number of nitro-haloid derivatives have been procured by Griess's method from nitro-haloid-amido-derivatives of benzene and its homologues.

A very large number of nitro-haloid derivatives of benzene and its homologues have been obtained by these various methods, but it will be impossible to give here more than a general account of their formation and properties. With very few exceptions they are crystalline substances, insoluble, or nearly so, in water, but soluble in alcohol, ether, benzene, &c. In most cases the bromo-derivatives have been more completely examined than either the chloro- or iodo- derivatives.

(1352) NITRO-HALOID DERIVATIVES OF BENZENE. *Nitro-monohaloid derivatives.*—Chloro- bromo- and iodobenzene each furnish a mixture of the *para-* and *orthomononitro*-derivatives on treatment with fuming nitric acid; the para-derivative is always the main product, but a relatively larger proportion of the ortho-derivative appears to be formed, the more violent the treatment to which the haloid benzene derivative is submitted: thus the best yield of orthonitrobromobenzene is obtained by adding the bromobenzene to nitric acid of the sp. gr. 1·5 heated to 90°—95° (194°—203° F.) (Zincke and Walker, *ibid.* v. 114). Moreover, iodobenzene appears to furnish relatively the largest amount of the orthonitro-derivative, as much as 40 per cent. of the product consisting under favourable conditions of orthonitroiodobenzene (Körner). Metanitro-chloro, bromo- and iodobenzene may be obtained by Griess's method from the metanitraniline, $C_6H_4.NO_2.NH_2$, formed on partially reducing metadinitrobenzene. Metanitrochlorobenzene may also be procured by chlorinating nitrobenzene.

Paranitrochlorobenzene is not altered by boiling fuming nitric acid, but on warming with a mixture of fuming nitric and sulphuric acid it furnishes, as *sole* product, *orthoparadinitrochlorobenzene* ($Cl : NO_2 : NO = 1 : 2 : 4$); paranitrobromo- and -iodobenzene furnish corresponding compounds. On similar treatment, or even on warming with fuming nitric acid, orthonitrochlorobenzene also furnishes orthoparadinitrochlorobenzene, but a small quantity of an isomeric *diorthonitrochlorobenzene* ($Cl : NO_2 : NO_2 = 1 : 2 : 6$), is simultaneously produced; orthonitrobromo- and -iodobenzene yield similar mixtures. The amount of diortho-derivative produced is always small (6 to 7 per cent. of the total product in the case of orthonitroiodobenzene according to Körner), and appears to be less, the more energetic the reaction. Metanitrobromobenzene also furnishes a mixture of isomeric dinitrobromobenzenes on nitration with a mixture of nitric and sulphuric acids, the chief product being a *parametadinitrobromobenzene* ($Br : NO_2 : NO_2 = 1 : 3 : 4$) (Körner).

The melting points (° Cent.) of the various nitro-derivatives of chloro- bromo- and iodobenzene are given in the following table:

—	chlorobenzene.	bromobenzene.	iodobenzene.	Constitution, the halogen being in the position 1.
Paranitro-	83°	125°·5	171°·4	1 : 4
Metanitro-	48°	56°·4	(?) 36°	1 : 3
Orthonitro-	15°	43°	49°·4	1 : 2
Orthoparadinitro- ...	53°·4	75°·3	88°·5	1 : 2 : 4
Diorthodinitro- ...	43°	—	113°·7	1 : 2 : 6
Parametadinitro- ...	—	59°·4	—	1 : 3 : 4

Nitro-dihaloid derivatives.—By the action of fuming nitric acid on *para*-dibromobenzene a single mononitro-derivative is produced; but *meta*- and *ortho*-dibromobenzene furnish two isomeric mononitro-derivatives, of one of which, however, relatively only a very small quantity is produced in each case. The chief product from metadibromobenzene is the modification $NO_2 : Br : Br : = 1 : 2 : 4$, and the accessory product the modification $NO_2 : Br : Br = 1 : 2 : 6$; a third nitrometadibromobenzene ($NO_2 : Br : Br = 1 : 3 : 5$) is obtained from dibromopara- and dibromorthonitraniline by displacing the NH_2 group by hydrogen. The chief nitration product from orthodibromobenzene is the modification $NO_2 : Br : Br = 1 : 3 : 4$. The isomeric dichlorobenzenes behave similarly. Paradiiodobenzene, however, is converted by nitric acid into paranitroiodobenzene, one of the atoms of iodine being displaced by the NO_2 group; but metadiiodobenzene yields a mononitro-derivative. The melting points (° Cent.) of these various derivatives are given in the following table:

—	dichloro-benzene	dibromobenzene.	diiodobenzene.	Constitution, the NO_2 group being in the position 1.
Nitropara-	54°·6	85°·4	—	1 : 2 : 5
Nitrometa-	32°·2	61°·6	168°·4	1 : 2 : 4
Nitrometa-	—	82°·6	—	1 : 2 : 6
Nitrometa-	65°·4	104°·5	—	1 : 3 : 5
Nitroortho-	43°	58°	—	1 : 3 : 4
Nitroortho-	—	—	—	1 : 2 : 3

On treatment with a mixture of nitric and sulphuric acid these nitrodibromobenzenes, &c., are more or less readily converted into dinitro-derivatives; but very few of these latter have as yet been carefully examined.

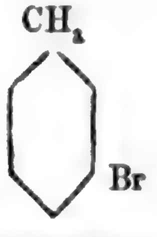
Nitro-trihaloid derivatives.—By the action of fuming nitric acid on 1 : 3 : 4 tribromobenzene a mixture of mononitro-derivatives is produced, consisting chiefly of the modification $NO_2 : Br : Br : Br = 1 : 2 : 4 : 5$, together with a small quantity of the modification $NO_2 : Br : Br : Br = 1 : 2 : 5 : 6$; a third nitrometatribromobenzene ($NO_2 : Br : Br : Br = 1 : 2 : 3 : 5$) is obtained by displacing the NH_2 group in dibromorthonitraniline by bromine. By heating with a large excess of a mixture of fuming nitric and fuming sulphuric acid the 1 : 2 : 4 : 5 nitrometatribromobenzene is converted into a dinitro-derivative. A nitroorthotribromobenzene (NO_2 : Br : Br : Br = 1 : 3 : 4 : 5) is obtained by displacing the NH_2 group in dibromoparanitraniline by bromine; it is uncertain whether this is the compound formed by nitrating orthotribromobenzene, or whether the product is the modification NO_2 : Br : Br : Br = 1 : 2 : 3 : 4. By the action of nitric acid of sp. gr. 1·54 paratribromobenzene is very readily converted into a dinitro-derivative, but by careful treatment with acid of the sp. gr. 1·52, in presence of a small quantity of acetic acid, it furnishes the mononitro-derivative NO_2 : Br : Br : Br = 1 : 2 : 4 : 6 (Richter, *Deut. chem. Ges. Ber.*, viii. 1426); by the action of a mixture of sulphuric and nitric acids, paratribromobenzene is finally converted into a trinitro-derivative. The melting points (° Cent.) of the mono- and dinitrotribromobenzenes are as follows:

	M. P.	Constitution, NO_2 in the pos. 1.		M. P.
Nitroparatribromobenzene	125°	1 : 2 : 4 : 6	Dinitroparatribromobenzene	192°
Nitroorthotribromobenzene	112°	1 : 3 : 4 : 5	Dinitroorthotribromobenzene	162°·4
„ „ „	—	1 : 2 : 3 : 4	—	—
Nitrometatribromobenzene	93°·5	1 : 2 : 4 : 5	Dinitrometatribromobenzene	135°·6
„ „ „	119°·5	1 : 2 : 3 : 5		
„ „ „	does not melt at 187°	1 : 2 : 5 : 6		

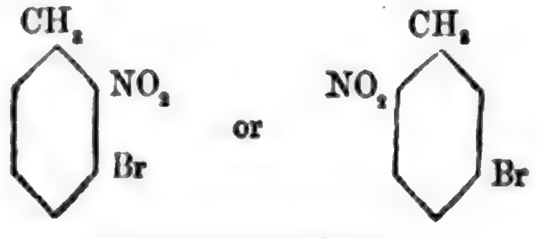
(1353) NITRO-HALOID DERIVATIVES OF TOLUENE.—Our knowledge of the nitro-haloid derivatives of toluene, and indeed of the homologues of benzene generally, is extremely deficient, and only in a limited number of cases are sufficient data at our disposal to enable us to infer their constitution.

On treatment with fuming nitric acid, *parabromotoluene* is converted into a mixture of isomeric nitrobromotoluenes; the main product is solid, and melts at 43° (109°·4 F.). When reduced, it furnishes a bromotoluidine, $C_6H_3Br.NH_2.CH_3$, which yields orthotoluidine on treatment with sodium amalgam and water (Wroblevsky). These observations show that crystalline nitroparabromotoluene has the constitution CH_3 : NO_2 : Br = 1 : 2 : 4, which is confirmed by its formation, by Greiss's method, from the nitrotoluidine from paraorthonitrotoluene (Beilstein and Kuhlberg); the liquid isomeride is therefore the modification CH_3 : NO_2 : Br = 1 : 3 : 4. Parachlorotoluene also yields two isomeric nitro-derivatives.

Metabromotoluene furnishes only a single nitro-derivative, which melts at 54° (129°·2 F.) (Grete, *Ann. Chem. Pharm.*, clxxvii. 245). The NO_2 group in this compound is in the ortho-position relatively to the CH_3 group, since the bromotoluidine obtained from it by reduction is identical with the bromotoluidine prepared from orthotoluidine; it is not known, however, which of the following figures represents nitrometabromotoluene:



Metabromotoluene.



Nitrometabromotoluene.

By the action of a mixture of concentrated nitric and sulphuric acids metabromotoluene is converted into a dinitro-derivative melting at about 103° (217°·4 F.).

The behaviour of pure *orthobromotoluene* on nitration has not yet been ascertained.

When (o–1) chlorotoluene or benzylic chloride is added to fuming nitric acid, it is converted into paranitro (o–1) chlorotoluene, which melts at 71° (159°·8 F.); a small quantity of an oily product is also produced, which is perhaps the isomeric orthonitro-derivative. Paranitro(o–1)chlorotoluene or paranitrobenzylic chloride is readily oxidized to paranitrobenzoic acid; and when digested with an alcoholic solution of potassic acetate, it is converted into paranitrobenzylic acetate, $C_6H_4.NO_2.CH_2(C_2H_3O_2)$.

(1354) ACTION OF AMMONIA AND ALKALIES ON THE NITRO-HALOID DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.—Although those haloid derivatives of the hydrocarbons of the benzene series which contain the halogen in the C_6 group are extremely stable substances, and do not exhibit the least tendency to enter into reactions of double decomposition, their nitro-derivatives frequently prove less refractory. Thus many of them on treatment with an alcoholic solution of ammonia exchange one and sometimes two atoms of halogen for one or two NH_2 groups. In some cases this action takes place at the ordinary atmospheric temperature, in others it is necessary to heat more or less strongly. The nitrochloro-derivatives appear to be more readily acted upon than the corresponding nitrobromo-, and the nitrobromo- more readily than the corresponding nitroiodo- derivatives; for example, dinitrochlorobenzene, $C_6H_3Cl(NO_2)_2$, melting at 53°·4 (128°·1 F.), is completely converted into dinitraniline, $C_6H_3.NH_2.(NO_2)_2$, within twenty-four hours, when merely placed in contact with an alcoholic solution of ammonia, whereas the corresponding dinitrobromobenzene requires eight days or more for its complete conversion into dinitraniline, and the corresponding dinitroiodobenzene is still in part unchanged, even after many months of contact with the ammonia solution (Körner).

In two remarkable instances Körner has observed the displacement of the NO_2 group by the NH_2 group by the action of ammonia on nitro-haloid derivatives. Thus when β-dinitroparadichlorobenzene, $C_6H_2Cl_2(NO_2)_2$, is heated with an alcoholic solution of ammonia to 150°—160° (302°—320° F.), it is converted into a *nitrodichloramidobenzene*, $C_6H_2Cl_2.NO_2.NH_2$, the NO_2 group being eliminated as ammonic nitrite, which then becomes resolved into nitrogen and water, thus:

$$C_6H_2Cl_2(NO_2)_2 + 2NH_3 = C_6H_2Cl_2.NO_2.NH_2 + N_2 + 2OH_2.$$

Similarly, by heating metaparadinitrobromobenzene to about 180° (356° F.) with ammonia solution, it is converted into a *bromonitroamidobenzene* ($Br : NH_2 : NO_2 = 1 : 3 : 4$).

Certain of the nitro-haloid derivatives are converted into *phenol* derivatives by heating with a more or less concentrated aqueous solution of potassic hydrate. Thus, by heating orthoparadinitroiodobenzene with a dilute solution of potassic hydrate, *potassium a-dinitrophenol* is produced :

$$C_6H_3I(NO_2)_2 + 2KHO = C_6H_3(NO_2)_2.OK + KI + OH_2.$$

Similarly, dinitrometadibromobenzene, $C_6H_2Br_2(NO_2)_2$, is converted into the potassium derivative of *dinitrometabromophenol*, $C_6H_2Br(NO_2)_2.OH$. This reaction, however, is not so frequently applicable as that with ammonia.

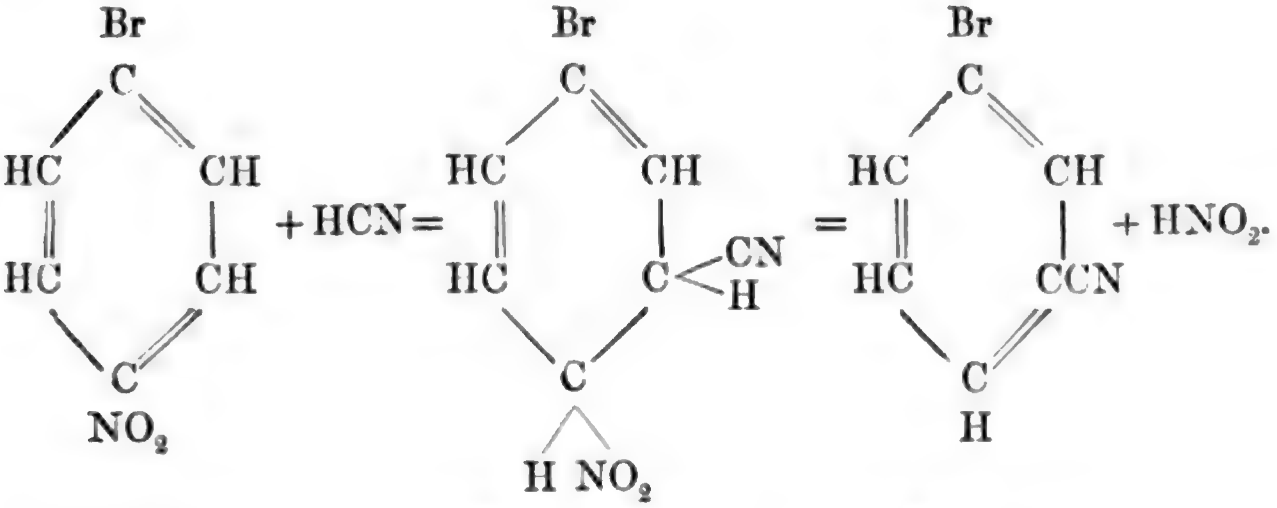
It is found (at least in the case of the di- and tri-derivatives) that it is not possible to displace an atom of halogen by NH_2 or OH, except it occupy the ortho- or para- position relatively to a nitro group. Thus *ortho*nitro- and *para*nitrobromobenzene may be converted into the corresponding nitroamidobenzenes, but ammonia is entirely without action on *meta*nitrobromobenzene.

(1355) ACTION OF POTASSIC CYANIDE ON NITRO-HALOID DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.—Von Richter has shown (*Deut. chem. Ges. Ber.*, iv. 21, 461, 553 ; v. 422 ; vii. 1145 ; viii. 1418) that when certain of the nitro-haloid derivatives of benzene and its homologues are heated with an alcoholic solution of potassic cyanide, and the product boiled with alkali, haloid derivatives of acids of the benzoic series are obtained. At first sight the natural interpretation of this result would seem to be that the NO_2 group is displaced by the CN group, and that this, by the action of water in presence of an alkali, is then resolved into COOH and ammonia ; for instance, when paranitrobromobenzene is converted into a bromobenzoic acid by this process, it might be supposed that the following reactions took place :

$$\underset{\text{Nitrobromobenzene.}}{C_6H_4Br.NO_2} + KCN = \underset{\text{Cyanobromobenzene.}}{C_6H_4Br.CN} + KNO_2 :$$

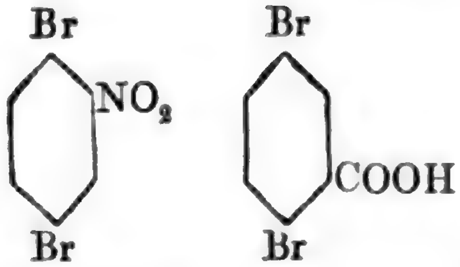
$$\underset{\text{Cyanobromobenzene.}}{C_6H_4Br.CN} + OH_2 = \underset{\text{Bromobenzoic acid.}}{C_6H_4Br.COOH} + NH_3.$$

This, however, does not seem to be the case ; for whereas the products formed by the action of ammonia or alkalies on nitro-haloid derivatives of benzene and its homologues *always* belong to the *same* isomeric series as the parent substances, *para*nitrobromobenzene, for example, being converted into *para*nitraniline, and *ortho*nitrobromobenzene into *ortho*nitraniline, Richter finds that the acids obtained by his method do not belong to the same isomeric series as the parent substances. Thus *para*nitrobromo- and chlorobenzene furnish respectively *meta*bromo- and chlorobenzoic acid, and *meta*nitrochloro-, bromo-, and iodobenzene are converted respectively into *ortho*chloro-, bromo-, and iodobenzoic acid. Richter explains this apparent anomaly by supposing that the first change which occurs is not a reaction of double decomposition, but that the nitro-haloid derivative enters into union with a molecule of hydrocyanic acid; the elements of a molecule of nitrous acid are then split off, and thus a cyano-haloid derivative is produced of a different isomeric series from that to which the nitro-haloid derivative belonged. This may be illustrated in the case of paranitrobromobenzene by the following figures:

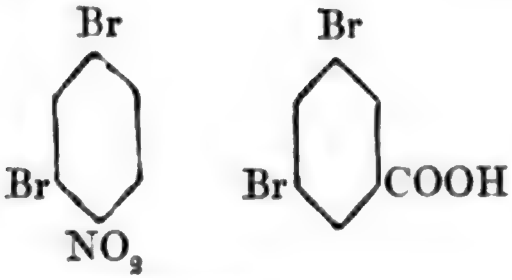


Paranitrobromobenzene. Additive compound with Hydrocyanic acid. Metacyanobromobenzene.

From the examination of the behaviour of a number of nitrohaloid derivatives, Richter concludes that in no case does the action take place when the NO_2 group is in the *ortho*-position (1 : 2) relatively to the halogen. Thus, although the crystalline nitroparabromotoluene ($CH_3 : NO_2 : Br = 1 : 2 : 4$) may be converted into a bromotoluic acid ($CH_3 : COOH : Br = 1 : 3 : 4$), the isomeric liquid modification (1 : 3 : 4) is not acted upon. Nitro*para*dibromobenzene enters into reaction with potassic cyanide when the two are heated together in alcoholic solution to 120°—140° (248°—284° F.); the isomeric nitro*meta*dibromobenzene, however, is only acted upon at about 250° (482° F.): in this way dibromobenzoic acids are produced, the relations of which to the parent substances are probably expressed by the following figures:



Nitroparad ibromobenzene.



Nitrometadibromobenzene.

Nitro-1 : 3 : 5-tribromobenzene and nitro-1 : 2 : 4 : 6-tetrabromobenzene are not attacked by an alcoholic solution of potassic cyanide.

(1356) GENERAL REVIEW AND SUMMARY OF THE ACTION OF REAGENTS ON BENZENE AND ITS HOMOLOGUES.—We have seen that although isomeric compounds are never formed by the displacement of a single atom of hydrogen in benzene by the halogens, NO_2, &c., isomerides are often produced from these mono-substitution derivatives of benzene. As far as we have yet gone, only those mono-substitution derivatives have been discussed which are formed by the introduction of CH_3 and radicles of the form C_nH_{2n+1}, the halogens, NO_2, or CN in place of hydrogen; but many others are known which will be described hereafter, together with the more important of their derivatives (see phenol, benzoic acid, and aniline). It will be of interest, however, at this stage to compare together the di-derivatives which result from the action of various reagents on all the known mono-substitution derivatives of benzene, leaving for description later on, the higher derivatives formed by the displacement of more than two atoms of hydrogen in benzene. In the following table the nature of the mono-derivative is denoted (column 1) simply by the radicle or side chain which is introduced into benzene in place of an atom of hydrogen, the figures in the columns to the right indicating the series to which the di-derivatives produced by the action of the halogens, nitric acid, or sulphuric acid belong; the main product if two or more isomeric substances result, is denoted by larger figures, and the accessory product or products by smaller figures, the radicle of the mono-derivative being always understood to occupy the position 1.

In a large number of cases the *para*-diderivative is the chief product, although the *ortho*-derivative is usually produced simultaneously: the relative proportions in which these two are formed being largely dependent upon the conditions under which the action takes place. It would seem, however, that the more care-

The radicle which displaces an atom of hydrogen in benzene forming the mono-derivative.	Series to which the derivative belongs, resulting from the introduction of				
	Cl	Br	I	NO_2	SO_3H
CH_3	**1 : 4** 1 : 2	**1 : 4** 1 : 2 1 : 3	?	**1 : 4** **1 : 2** *	**1 : 4** 1 : 2
CH_2Cl $CHCl_2$ CCl_3	**1 : 4**	?	?	**1 : 4**	?
Cl...................	**1 : 4** 1 : 2	**1 : 4** 1 : 2	?	**1 : 4** 1 : 2	**1 : 4**
Br	Displaces the bromine.	**1 : 4** 1 : 2	?	**1 : 4** 1 : 2	**1 : 4**
I	Displaces the iodine.	Displaces the iodine.	**1 : 4**	**1 : 4** 1 : 2	**1 : 4**
OH	**1 : 4** 1 : 2	**1 : 4** 1 : 2 1 : 3	**1 : 4** 1 : 2 1 : 3	**1 : 4** **1 : 2** *	**1 : 4** 1 : 2
NH_2................	**1 : 4**	**1 : 4** 1 : 2 ?	**1 : 4**	**1 : 4** 1 : 2	**1 : 4**
$CH_2.COOH$ ...	**1 : 4**	**1 : 4**	?	**1 : 4** 1 : 2	?
$CH{:}CH.COOH$	?	?	?	**1 : 4** 1 : 2	?
$CO.CH_3$	?	?	?	**1 : 4** 1 : 2	?
NO_2	**1 : 3**	Displaces the nitro-group.	Displaces the nitro-group.	**1 : 3** 1 : 2 1 : 4	**1 : 3** 1 : 2 1 : 4
SO_3H	?	**1 : 3**	?	**1 : 3** 1 : 2 1 : 4	**1 : 3** 1 : 4
COOH............	**1 : 3**	**1 : 3**	**1 : 3**	**1 : 3** 1 : 2 1 : 4	**1 : 3** 1 : 4
COH	?	?	?	**1 : 3**	?
CN	?	?	?	**1 : 3**	?
$SO_2.C_6H_5$.........	?	?	?	**1 : 3**	?

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* According to Rosenstiehl (p. 324), paranitrotoluene is the main produc when the nitration is effected by a large excess of acid (5 pts. of sp. gr. 1·5 to 1 of toluene) at a relatively high temperature (40° C.), but orthonitrotoluene i chiefly produced if a relatively small amount of acid be taken (equal parts o

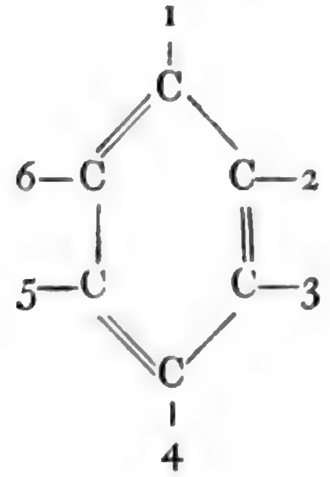
fully and gradually the displacement is effected the less of the ortho-derivative is produced, and it is noteworthy that when the para-derivative is the main product, the meta-derivative is very seldom formed. In other instances again, and especially in the presence of those groups which usually confer an acid character upon the compounds which contain them (NO_2, COOH, SO_3H), the meta-di-derivative is either the sole product, or is obtained together with a relatively very small quantity of the para-, or the para- and ortho-derivatives.

Attention has already been called to the fact that the displacement of halogen in the nitro-haloid derivatives by NH_2 or OH only takes place (in the case of the di- and tri-derivatives of benzene) when the halogen is in the *ortho-* or *para-* position relatively to the NO_2 group. Certain of the nitro-haloid-amido-derivatives, however, furnish nitro-haloid derivatives of the phenols (*i.e.* the NH_2 group is displaced by the OH group) when they are submitted to the action of potassic hydrate solution; thus:

$$C_6H_3Cl.NO_2.NH_2 + KHO = C_6H_3Cl.NO_2.OH + NH_3;$$

and the reverse change may often be effected by heating the phenol derivatives—or rather the compounds derived from them by displacing hydrogen in the OH group by CH_3 or C_2H_5—with ammonia. These reactions, again, only take place when the NH_2 and OCH_3 groups, &c., are in either the *para-* or *ortho-* position relatively to the NO_2 group.

It is evident that Kekulé's benzene symbol scarcely affords a satisfactory representation of these facts:



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acid and toluene), and the nitration be effected at a lower temperature (10° C.). With phenol, however, the case is different, for Körner states that paranitrophenol is mainly produced on nitrating phenol in the cold, but that orthonitrophenol prevails if the action takes place at higher temperatures.

since it does not in any way indicate that a given radicle in the position 1 will have a certain influence in favouring the displacement of an atom of hydrogen in the positions 2 (or 6) and 4, and that it will tend to prevent, or at least in no way favour, the displacement of the atoms of hydrogen in the position 3 (or 5): that is to say, it does not account for the simultaneous formation of para- and ortho-derivatives almost or completely to the exclusion of meta-derivatives; nor does it indicate that a NO_2 group in the position 1 will render possible the displacement of an atom of halogen in the position 2 (and 6) or 4, but that it will not in the least favour its displacement if it is in the position 3 (or 5). On the contrary, it seems to indicate that whatever influence the radicle in the position 1 may have upon the radicles in the positions 2 (or 6), 3 (or 5) and 4, the influence exercised upon the radicles in the position 3 (or 5) will be in a measure intermediate between that exercised upon those in the positions 2 (or 6) and 4, which we have seen is not the case. Of the numerous symbols to represent benzene which have been proposed, however, none are able to express the relations above indicated, and at the same time to afford a satisfactory representation of the facts which *can* be adequately demonstrated with the aid of Kekulé's symbol; and we may say, in short, that Kekulé's symbol, although by no means affording an explanation of all the known facts in connexion with benzene and its homologues, yet does exhibit them far more perfectly than any other, and is probably the best graphic expression that can be devised, considering the present state of our knowledge of the subject.*

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* The reader is requested to cancel the passage on p. 263, line 7 to line 15, commencing—"but inasmuch" *to* "known reactions of benzene," the insertion of which is due to an oversight.—EDS.

§ VI. HYDROCARBONS OF THE C_nH_{2n-8} OR CINNAMENE SERIES.

The following members of this series have been obtained :

			B.P. ° Cent.
C_8H_8	Phenylethylene or Cinnamene	$CH.C_6H_5$ ‖ CH_2	146°
C_9H_{10}	α-Phenylpropylene or Methylphenylethylene	$CH.C_6H_5$ ‖ $CH.CH_3$	about 165°
	β-Phenylpropylene, Benzylethylene, or allylbenzene	$CH.CH_2.C_6H_5$ ‖ CH_2	about 155°
$C_{10}H_{12}$	α-Phenylbutylene or Ethylphenylethylene	$CH.C_6H_5$ ‖ $CH.C_2H_5$	180°
	β-Phenylbutylene or Phenethylethylene	$CH(CH_2.CH_2.C_6H_5)$ ‖ CH_2	176°–178°
	Naphthalene tetrahydride	—	205°

(1357) CINNAMENE OR PHENYLETHYLENE. *Cinnamol ; Styrolene* or *Styrol :* C_8H_8 or $H_2C{=}CH.C_6H_5$. — This hydrocarbon exists in small quantity ready formed in *liquid storax*, a soft viscid resin obtained from the *Liquidambar orientalis*, a tree resembling a plane, which grows in the south-western part of Asia Minor (Hanbury and Flückiger). It is extracted by distilling the resin with water containing sodic carbonate to retain cinnamic acid, when it passes over with the steam, and floats as an oil on the surface of the water in the receiver. It is produced synthetically when a mixture of benzene vapour and ethylene is passed through a red-hot tube, hydrogen being eliminated : $C_6H_6+C_2H_4=C_8H_8+H_2$. Benzene and acetylene under similar circumstances combine directly : $C_6H_6+C_2H_2=C_8H_8$; and acetylene alone, when strongly heated, yields the same hydrocarbon : $4C_2H_2=C_8H_8$ (Berthelot). A fourth method of formation is to heat the vapour of ethylbenzene to redness : $C_8H_{10}=C_8H_8+H_2$.

Cinnamene may be prepared from cinnamic acid by distilling it slowly, or by distilling an intimate mixture of one part of the acid with four of baric oxide, the reaction being similar to that which occurs when benzoic acid is distilled with excess of lime:

$$\underset{\text{Cinnamic acid.}}{C_8H_7.COOH} + BaO = \underset{\text{Cinnamene.}}{C_8H_8} + BaCO_3.$$

The monobromethylbenzene, $C_6H_5.CHBr.CH_3$, produced by the action of bromine on heated ethylbenzene, readily splits up into cinnamene and hydrobromic acid (Radziszewski, *Deut. chem. Ges. Ber.*, vi. 492). The best method of effecting this decomposition is to heat the bromide with an alcoholic solution of potassic hydrate to 180° (356° F.). In this instance metacinnamene is produced, which may be converted into cinnamene by distillation.

Cinnamene is a colourless mobile liquid, of high refractive power and pleasant aromatic odour, which boils at 146° (294°·8 F.), and does not solidify at −20° (−4° F.). During distillation, however, the liquid in the retort is apt to rise suddenly in temperature, and to be converted into *metacinnamene*. According to Berthelot (*Compt. Rend.*, lxiii. 518), the cinnamene prepared from cinnamic acid is not identical with that existing in storax; the former being optically inactive, whilst the latter turns the plane of polarization to the left. Van t' Hoff has shown, however (*Deut. chem. Ges. Ber.*, ix. 5), that the two products are identical, and that the optical activity of the latter is due to the presence of a small quantity of another substance.

Cinnamene, like the olefines, combines readily with a molecule of chlorine, bromine, or iodine. *Cinnamene dibromide*, $C_9H_8Br_2$, which is most conveniently prepared by adding bromine to a solution of the hydrocarbon in chloroform, is identical with the dibromethylbenzene obtained by the action of bromine on ethylbenzene (1339). By heating alone, or with an alcoholic solution of potassic hydrate, cinnamene dichloride and dibromide are converted into *chlorocinnamene*, $C_6H_5.CH{=}CHCl$, and *bromocinnamene*,* $C_6H_5.CH{=}CHBr$, respectively: they are colourless heavy liquids, which undergo decomposition when distilled, and their vapour exerts an irritating action upon the eyes. By heating the phenyldichloro- and phenyldibromopropionic acids, and phenylchloro- and phenylbromolactic acids with water, isomeric chloro- and bromocinnamenes, $C_6H_5.CCl{=}CH_2$ and $C_6H_5.CBr{=}CH_2$ are obtained: these are colourless oils, having a pleasant hyacinth odour, which boil without decomposition at 199° (390°·2 F.) and 228° (442°·4 F.) respectively (Glaser, *Ann. Chem. Pharm.*, cliv. 1641).

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* According to Radziszewski (*Deut. chem. Ges. Ber.*, vi. 492), the isomeric compound, $C_6H_5.CBr{=}CH_2$, is obtained when cinnamene dibromide is decomposed by heating with water in sealed tubes at 190° (374° F.).

When cinnamene is gradually added to fuming nitric acid, the greater part becomes resinified, but a portion is converted into *nitrocinnamene*, $C_8H_7.NO_2$; it crystallizes in large prisms, having a pungent aromatic odour.

Cinnamene is readily converted by oxidation into benzoic acid.

(1358) ***Metacinnamene*** : $(C_8H_8)_n$.—Cinnamene is slowly converted into this body at the ordinary temperature, and is rapidly polymerized when heated in sealed tubes to 200° (392° F.). Metacinnamene is an amorphous, colourless solid of high refracting power, and is destitute of smell and taste. It is quite transparent, and softens on the application of heat, when it may be drawn out into threads; on distillation, it is reconverted into cinnamene. It is insoluble in water and in alcohol, and is but very sparingly soluble in ether; it yields benzoic acid on oxidation.

(1359) α-PHENYLPROPYLENE : $C_6H_5.HC{=}CH.CH_3$; METHYLPHENYLETHYLENE.—This hydrocarbon is obtained in small quantity together with phenylpropylic alcohol by the action of sodium amalgam on a warm aqueous solution of cinnamic or styrylic alcohol, $C_6H_5.HC{=}CH.CH_2.OH$ (Fittig, *Deut. chem. Ges. Ber.*, vi. 214). It is more readily prepared by submitting propylbenzene heated to about 150° (302° F.) to the action of a molecule of bromine, and distilling the product (Radziszewski, *ibid.* vii. 140; ix. 260):

$$\underset{\text{Bromopropylbenzene.}}{C_6H_5.CHBr.CH_2.CH_3} = \underset{\text{Phenylpropylene.}}{C_6H_5.HC{=}CH.CH_3} + HBr.$$

It is a colourless liquid boiling at about 165° (329° F.); it combines directly with a molecule of bromine to form the compound, $C_9H_{10}Br_2$, which crystallizes in colourless plates, melting at 66°·5 (151°·7 F.) (Rügheimer, *Ann. Chem. Pharm.*, clxxii. 129).

Phenylchloropropylene; Cinnamic chloride: $C_6H_5.HC{=}CH.CH_2Cl$, prepared by treating cinnamic alcohol with dry hydrochloric acid, is a heavy oily liquid, which cannot be distilled without decomposition. ***Phenyliodopropylene***, or ***cinnamic iodide***, C_9H_9I, prepared by the action of phosphorus iodide on the same alcohol, closely resembles the chloride. ***Phenylcyanopropylene***, ***cinnamic*** or ***styrylic cyanide***, $C_9H_9.CN$, is produced by heating the iodide at 100° (212° F.) with an alcoholic solution of potassic cyanide. It is a yellowish oil, which is insoluble in water, sparingly soluble in alcohol, but readily so in ether (Ramdohr, *Zeits. Pharm.*, 1858, 113).

(1360) β-PHENYLPROPYLENE or ALLYLBENZENE : $C_6H_5.CH_2.CH{=}CH_2$.—The attempts to prepare this hydrocarbon from bromobenzene and allylic bromide by the action of sodium have been unsuccessful. Chojnacki, however, states (*Compt. Rend.*, lxxvi. 1413) that a small quantity of allylbenzene, boiling at about 155° (311° F.), is formed, when a mixture of benzene and allylic iodide is heated with zinc powder.

(1361) α-PHENYLBUTYLENE : $C_6H_5.HC{=}CH.C_2H_5$; ETHYLPHENYLETHYLENE.—This hydrocarbon is obtained by distilling the bromo-derivative formed by the action of bromine on boiling α-butylbenzene:*

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* α-Butylbenzene is obtained by the action of sodium on a mixture of

$$\underset{\text{Bromo-α-butylbenzene.}}{C_6H_5.CHBr.CH_2.CH_2.CH_3} = HBr + \underset{\text{α-Phenylbutylene.}}{C_6H_5.CH{=}CH.CH_2.CH_3}.$$

It boils at 186° (366°·8 F.), and furnishes a crystalline dibromide, $C_{10}H_{12}Br_2$, which melts at 70°—71° (158°—159°·8 F.) (Radziszewski, *Deut. chem. Ges Ber.*, ix. 260).

(1362) β-PHENYLBUTYLENE: $H_2C{=}CH(CH_2.CH_2.C_6H_5)$; PHENETHYLETHYLENE, is formed along with diallyl and dibenzyl, when a mixture of benzylic chloride and allylic iodide in ethereal solution is digested with sodium (Aronheim, *loc. cit.*, v. 1068):

$$\underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} + \underset{\text{Allylic iodide.}}{CH_2I.CH{=}CH_2} + 2Na = \underset{\text{β-Phenylbutylene.}}{C_6H_5.CH_2.CH_2.CH{=}CH_2} + NaI + NaCl$$

It is a colourless liquid boiling at about 177° (350°·6 F.); it forms an oily compound, $C_{10}H_{12}Br_2$, when treated with bromine.

Naphthalene tetrahydride: $C_{10}H_{12}$.—This compound is produced by heating naphthalene, $C_{10}H_8$, (10 grms.) with amorphous phosphorus (3 grms.) and hydriodic acid (9 grms. of a solution boiling at 127° C.) in sealed tubes for 6—8 hours at 220°—250° (428°—482° F.). It is a liquid of peculiar odour, which boils at 205° (401° F.). On passing its vapour through a red-hot tube, it is resolved into naphthalene and hydrogen; on treatment with oxidizing agents it is converted into phthalic acid far more readily than naphthalene. It is converted by concentrated sulphuric acid into a sulphonic acid, $C_{10}H_{11}.SO_3H$, and bromine also forms with it substitution derivatives, which readily decompose on distillation (Græbe, *ibid.* v. 678). Naphthalene tetrachloride, $C_{10}H_8Cl_4$, and the chloronaphthalene tetrachlorides may be regarded as substitution derivatives of this hydrocarbon.

§ VII. HYDROCARBONS OF THE C_nH_{2n-10} OR ACETENYLBENZENE SERIES.

(1363) ACETENYLBENZENE OR PHENYLACETYLENE: C_8H_6 or $C_6H_5.C{\equiv}CH$, which is the only member of the series at present known, may be produced by heating cinnamene dibromide, or the bromocinnamene prepared from it, with an alcoholic solution of potassic hydrate to 120° (248° F.) (Glaser, *Ann. Chem. Pharm.*, cliv. 137) (see footnote, p. 369):

$$\underset{\text{Bromocinnamene.}}{C_6H_5.HC{=}CHBr} + KHO = \underset{\text{Acetenylbenzene.}}{C_6H_5.C{\equiv}CH} + KBr + OH_2;$$

or by passing it over lime at a low red heat (Radziszewski, *Deut. chem. Ges. Ber.*, vii. 140). The isomeric bromocinnamene does not furnish acetenylbenzene when similarly treated, but by dissolving it in ether, adding sodium, and passing a current of

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benzylic chloride and propylic bromide without the addition of ether; it boils at 180° (356° F.) (Radziszewski). β-Butylbenzene, according to the same observer, boils at 170°—172° (338°—341°·6 F.) (compare 1302).

carbonic anhydride into the solution, the sodic salt of phenylpropiolic acid is obtained, and on heating this acid with water to 120° (248° F.) it splits up into acetenylbenzene and carbonic anhydride (Glaser). It appears probable that under the conjoint influence of the sodium and carbonic anhydride the bromocinnamene is resolved into hydrobromic acid and acetenylbenzene, the latter at once undergoing conversion into sodic propiolate; thus:

$$\underset{\text{Bromocinnamene.}}{2C_6H_5.CBr{=}CH_2} + 2Na = \underset{\text{Acetenylbenzene.}}{2C_6H_5.C{\equiv}CH} + 2NaBr + H_2$$

$$\underset{\text{Acetenylbenzene.}}{2C_6H_5.C{\equiv}CH} + 2Na = \underset{\text{Sodium acetenylbenzene.}}{2C_6H_5.C{\equiv}CNa} + H_2$$

$$\underset{\text{Sodium acetenylbenzene.}}{C_6H_5.C{=}CNa} + CO_2 = \underset{\text{Sodic propiolate.}}{C_6H_5.C{\equiv}C.COONa.}$$

$$\underset{\text{Propiolic acid.}}{C_6H_5.C{\equiv}C.COOH} = \underset{\text{Acetenylbenzene.}}{C_6H_5.C{\equiv}CH} + CO_2.$$

Acetenylbenzene is most readily obtained from propiolic acid by distilling its baric salt mixed with sand.

According to Friedel (*Compt. Rend.*, lxvii. 1192), phenylacetylene is also obtained when the phenyldichlorethane formed by the action of phosphoric pentachloride on methylphenylketone is heated with an alcoholic solution of potassic hydrate* to 120° (248° F.):

$$\underset{\text{Methylphenylketone.}}{C_6H_5.CO.CH_3} + PCl_5 = \underset{\text{Phenyldichlorethane.}}{C_6H_5.CCl_2.CH_3} + POCl_3.$$

$$\underset{\text{Phenyldichlorethane.}}{C_6H_5.CCl_2.CH_3} + 2KHO = \underset{\text{Acetenylbenzene.}}{C_6H_5.C{=}CH} + 2KCl + 2OH_2.$$

Acetenylbenzene is a colourless liquid of peculiar aromatic odour and high refractive power, which boils at 140° (284 F.). It not only bears the same relation in composition to acetylene that cinnamene bears to ethylene, but like the former possesses the property of yielding precipitates with certain metallic solutions. Thus, with an ammoniacal solution of cuprous chloride, it gives a yellow precipitate of the composition $(C_8H_5)_2Cu_2$, and with the corresponding silver solution a light gray compound $(C_8H_5Ag)_2.Ag_2O$. The sodium derivative, C_8H_5Na, is formed on adding sodium to an ethereal solution of the hydrocarbon, hydrogen being simultaneously evolved: it is a white powder which absorbs oxygen rapidly when exposed to the air, becoming red-hot, and leaving a residue of carbon and sodic carbonate; it readily absorbs carbonic anhydride, forming sodic propiolate. When the cuprous derivative of phenylacetylene is agitated with an alcoholic solution of ammonia in presence of air, it is converted into *diphenyldiacetylene*:

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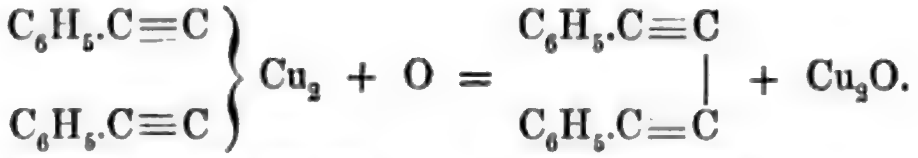
* According to Glaser, neither chlorocinnamene, $C_6H_5.CCl{=}CH_2$, nor the corresponding bromocinnamene is decomposed by an alcoholic solution of potassic hydrate even at 200° (392° F.): although they are partially resinified, no potassic chloride or bromide is separated. This result, therefore, appears somewhat remarkable, since the chlorocinnamene which is the first product of the action of potassic hydrate on phenyldichlorethane, doubtless has the formula $C_6H_5.CCl{=}CH_2$ (compare p. 369 and Engler, *Deut. chem. Ges. Ber.*, viii. 397).



$$\left.\begin{array}{l}C_6H_5.C\equiv C\\ \\ C_6H_5.C\equiv C\end{array}\right\}Cu_2 + O = \begin{array}{r}C_6H_5.C\equiv C\\ |\\ C_6H_5.C\equiv C\end{array} + Cu_2O.$$

Cuprous derivative of phenylacetylene. Diphenyldiacetylene.

§ VIII. HYDROCARBONS OF THE C_nH_{2n-12} OR NAPHTHALENE SERIES.

This series includes four hydrocarbons, but only one of them is of importance:

		B.P. ° Cent.
Naphthalene	$C_{10}H_8$	218°
Methylnaphthalene . .	$C_{10}H_7.CH_3$	232°
Ethylnaphthalene . . .	$C_{10}H_7.C_2H_5$	250°
Anthracene hexahydride .	$C_{14}H_{16}$	290°

(1364) NAPHTHALENE: $C_{10}H_8=128$.—This hydrocarbon is a constituent of the principal varieties of tar, but is most abundant in coal tar, particularly in that obtained from the London gasworks, where it frequently causes considerable inconvenience by partially stopping up the large cast-iron pipes used to convey the gas to different districts. It is thus frequently obtained in large colourless plates, which are nearly pure, or it may be obtained from the portion of the distillate from coal tar boiling at about 200° which becomes semi-solid on cooling, by pressing out the liquid portion and submitting the crystals to sublimation or crystallization from alcohol. In order to obtain it quite pure, however, it is necessary to heat it strongly with a small quantity of sulphuric acid, wash thoroughly, and then sublime it. Naphthalene is also produced by the decomposition at a red heat of benzene, toluene, cymene, and many other organic substances; and also when a mixture of ethylene with the vapour of cinnamene, anthracene, or chrysene is passed through a red-hot tube. β-Phenylbutylene dibromide when passed over lime heated to low redness is almost entirely converted into naphthalene (Aronheim) in the manner represented by the equation:

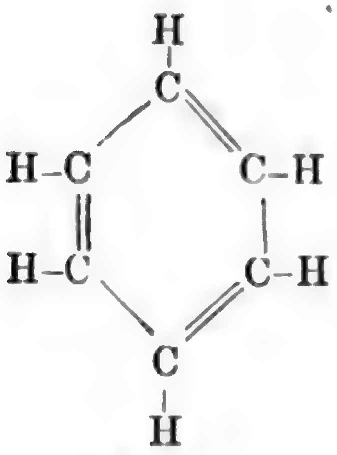
$$C_{10}H_{12}Br_2 + CaO = C_{10}H_8 + CaBr_2 + H_2 + OH_2.$$

According to Radziszewski, α-phenylbutylene dibromide (1361) also furnishes naphthalene when similarly treated.

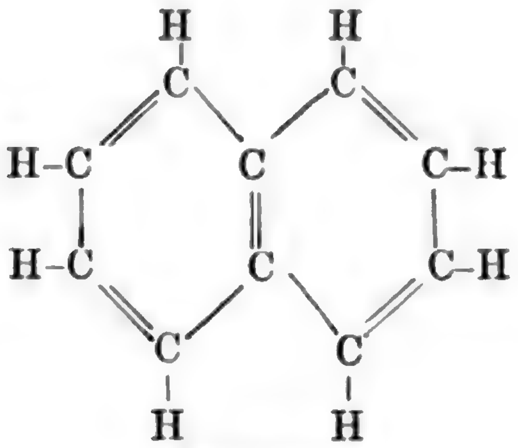
Naphthalene crystallizes in brilliant colourless rhombic plates, which feel unctuous to the touch, and have a pearly lustre. Its density is 1·1517 at 15° (59° F.): it melts at 79° (174°·2 F.) and boils at 218° (424°·4 F.). The odour of this hydrocarbon is peculiar, and its taste biting and somewhat aromatic. It gradually sublimes at the ordinary temperature, and rapidly passes over with the vapour of water. Naphthalene burns with a white smoky flame, although it is not readily kindled. It is insoluble in water, but is easily soluble in alcohol, ether, benzene, oil of turpentine, glacial acetic acid, and the fixed oils. Melted naphthalene absorbs air copiously, and gives it off again on solidification. It dissolves iodine, sulphur, phosphorus, and the sulphides of arsenic, antimony, and tin, as well as mercuric iodide, indigo, oxalic, succinic, and benzoic acids. Naphthalene combines with trinitrophenol or picric acid, forming the compound $C_{10}H_8 + C_6H_2(NO_2)_3.OH$. This compound may readily be prepared by mixing hot alcoholic solutions of trinitrophenol and the hydrocarbon, and may be recrystallized from alcohol or from benzene, but is slowly decomposed by boiling water, and rapidly by alkaline solutions; it crystallizes in stellate groups of yellow needles, which melt at 149° (300°·2 F.). Naphthalene is the only solid hydrocarbon whose cold saturated alcoholic solution is precipitated by trinitrophenol.

By oxidation with potassic permanganate, naphthalene is converted into *phthalic acid*, $C_6H_4(COOH)_2$; but by the action of chromic acid on naphthalene dissolved in glacial acetic acid, *naphthaquinone*, $C_{10}H_6O_2$, is produced (Groves, *Journ. Chem. Soc.*, xxvi. 209).

(1365) *Constitution of Naphthalene.*—In its general chemical behaviour naphthalene very closely resembles benzene, and it will be seen on reference to the following figures that the method usually adopted for representing these hydrocarbons graphically, indicates a close relationship between them:

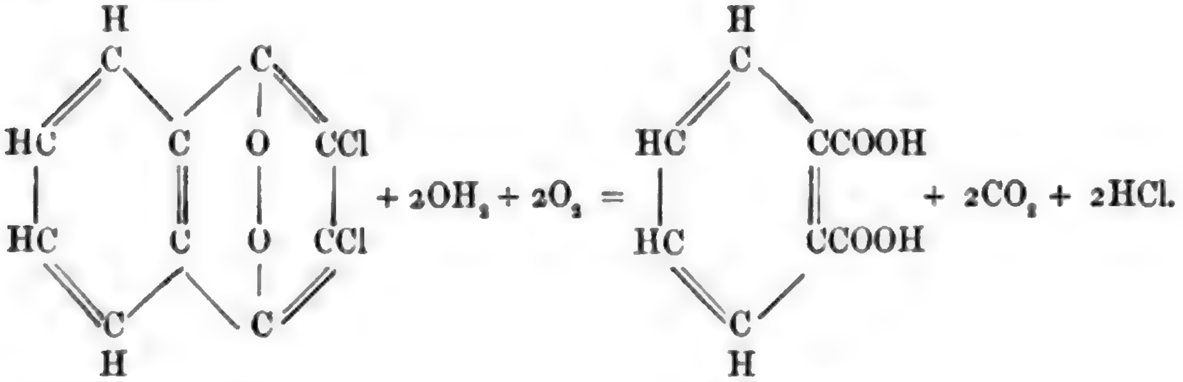


Benzene.



Naphthalene.

This symbol for naphthalene was suggested by Erlenmeyer in 1868 (*Ann. Chem. Pharm.*, cxxxvii. 346), but the proof that naphthalene may really be regarded as composed of two benzene-nuclei having two atoms of carbon in common, was first given by Græbe in 1869 (*ibid.* cxlix. 20). In the conversion of naphthalene into phthalic acid, only one of the benzene nuclei undergoes oxidation, but Græbe showed that either may be oxidized and phthalic acid obtained. Thus he found that dichloronaphthaquinone furnishes *phthalic acid* on oxidation, which is a proof that the two chlorine atoms and the two oxygen atoms are contained in the same nucleus, the nucleus containing them being destroyed by oxidation :



Dichloronaphthaquinone. Phthalic acid.

When, however, dichloronaphthaquinone is treated with phosphoric pentachloride, *pentachloronaphthalene* is produced; the two oxygen atoms being displaced by two chlorine atoms, whilst an atom of hydrogen in the second nucleus is also displaced by chlorine. On oxidizing this compound, *tetrachlorophthalic acid* is obtained, the nucleus which had undergone oxidation in the reaction previously mentioned, remaining intact in the second case, as shown in the accompanying graphic formulæ :*

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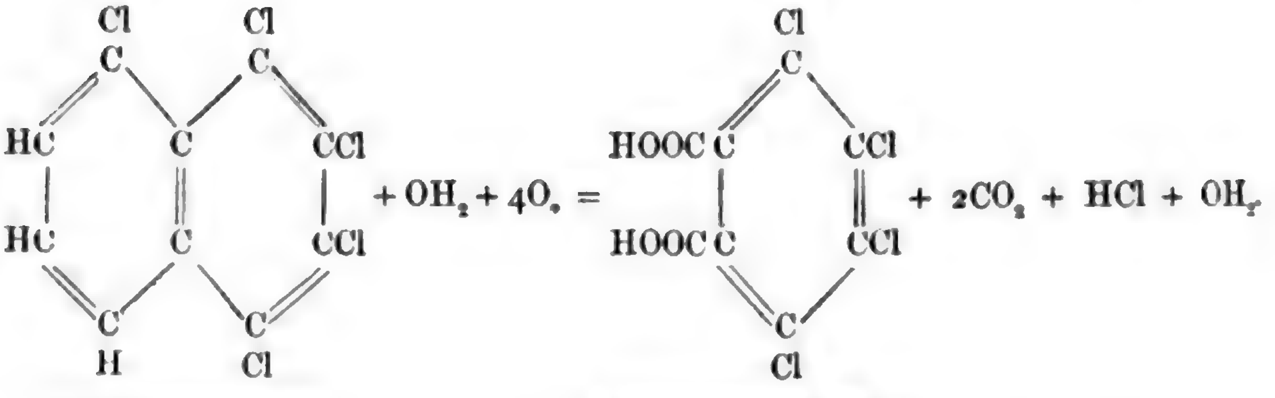
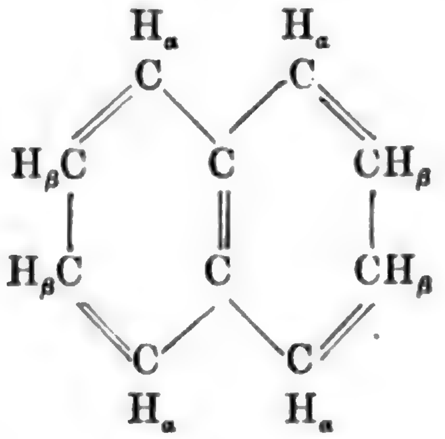
* It is perhaps scarcely necessary to point out that in representing naphthalene graphically we are entirely dependent upon the kind of symbol we assign to



Pentachloronaphthalene. Tetrachlorophthalic acid.

(1366) *Isomeric substitution derivatives of Naphthalene.*—Although benzene cannot yield isomeric mono-substitution derivatives, it will be evident on reference to the following figure that naphthalene can furnish *two* isomeric mono-substitution derivatives:



It will be seen that each of the four carbon atoms to which the four hydrogen atoms marked *a* are attached, is similarly related to the other nine carbon atoms, and the same is the case with the four marked β; the relation which the four marked *a* bear to the other carbon atoms is different, however, from that of the four marked β. It may be supposed, therefore, that isomeric derivatives may be formed, according as an atom of hydrogen attached to a carbon atom marked *a*, or to one marked β, is displaced. These two classes of isomeric mono-substitution derivatives of naphthalene are, for the sake of convenience, distinguished as *a* and β derivatives.

The action of the halogens and of nitric acid upon naphthalene appears to give rise to the formation of but a single mono-derivative, whilst by the action of sulphuric acid, a mixture of two isomeric ***naphthalene-a-*** and ***-β-sulphonic acids***, $C_{10}H_7.SO_3H$, is produced.

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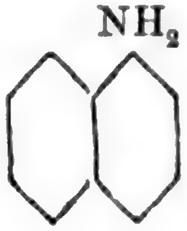
benzene, and that the objections urged against Kekulé's benzene symbol apply equally to Erlenmeyer's naphthalene symbol; as in the case of benzene, however, no more appropriate symbol has as yet been suggested.

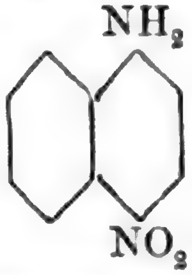
Although our knowledge of the naphthalene derivatives is as yet extremely imperfect, very few attempts having been made to establish the nature of the relationship which exists between them, a number of data are at our disposal which enable us to infer with much probability the constitution of the mono-, and even of some of the higher derivatives of naphthalene. Thus by the action of nitric acid, naphthalene is converted into *nitronaphthalene*, $C_{10}H_7.NO_2$, which furnishes *amidonaphthalene* or *naphthylamine*, $C_{10}H_7.NH_2$, on reduction; by converting the latter into *acetamidonaphthalene* or *acenaphthalide*, $C_{10}H_7.NH(C_2H_3O)$, and submitting this to the action of nitric acid, a mixture of isomeric mono-nitro-derivatives is obtained. The main product is converted, by boiling for a short time with an alcoholic solution of potassic hydrate, into an *amidonitronaphthalene*, $C_{10}H_6.NO_2.NH_2$, which melts at 191° (375°·8 F.), whilst the accessory product yields an isomeric substance which melts at about 159° (318°·2 F.). By displacing the NH_2 group by hydrogen in the amidonitronaphthalene melting at 191°, a nitronaphthalene is obtained identical with that directly prepared from naphthalene; it is thus proved that, whatever the position of the NO_2 group in nitronaphthalene and consequently of the NH_2 group in amidonaphthalene, the NO_2 group in amidonitronaphthalene has a similar position relatively to the two carbon atoms common to the two benzene nuclei.

By reducing the amidonitronaphthalene melting at 191°, a diamidonaphthalene is obtained which furnishes almost the theoretical amount of naphthaquinone on oxidation, and this naphthaquinone is found to yield phthalic acid on further oxidation with nitric acid (Liebermann, *Deut. chem. Ges. Ber.*, vi. 945; vii. 240; viii. 689; ix. 333). These observations show that the two oxygen atoms in naphthaquinone, and consequently the NH_2 group in diamidonaphthalene, and the NH_2 and NO_2 groups in the amidonitronaphthalene melting at 191°, are in the *same benzene nucleus*.

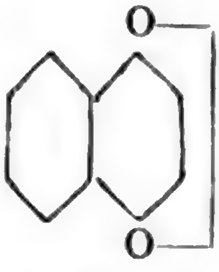
It is known that in ordinary quinone, $C_6H_4O_2$, the oxygen atoms are relatively in the para or 1 : 4 position, and although it is not absolutely proved, there is the very greatest probability that they are similarly placed in naphthaquinone (*see Quinones*); if, however, it be admitted that such is the case, these results show that, in amidonaphthalene, the NH_2 group displaces a hydrogen atom attached to one of the carbon atoms marked *a* in the above figure, because it is only when it is in that position that a second radicle can be introduced so as to occupy the para-position relatively to it. This will doubtless be better understood on reference to the following figures:*



α-Amidonaphthalene.



α-Nitro-α-amidonaphthalene.



Naphthaquinone.

The constitution of many other mono-derivatives of naphthalene may be traced in a similar manner. Thus by digesting the amidonitronaphthalene melting at 191° above mentioned with sodic hydrate solution, the amido-group is displaced by OH and a *mononitronaphtol*, $C_{10}H_6.NO_2.OH$, is obtained; on nitration, this latter is converted into a dinitronaphtol identical with that formed by nitrating the so-called α-naphtol, $C_{10}H_7.OH$. It therefore follows that α-naphtol is really a member of the α series of mono-derivatives of naphthalene; and since it is obtained by displacing the SO_3H group in the so-called α-naphthalenesulphonic acid by OH, it also follows that this sulpho-acid is an α derivative. The isomeric so-called β-sulphonic acid, and the naphtol and other compounds formed from it by simply displacing the SO_3H group are consequently members of the β series of isomeric mono-derivatives of naphthalene. By displacing the SO_3H group in naphthalene-α-sulphonic acid by chlorine, by the action of phosphoric pentachloride, a chloronaphthalene identical with that obtained by chlorinating naphthalene is produced: ordinary chloronaphthalene is therefore an α-derivative of naphthalene.†

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* We may conveniently represent naphthalene by two hexagons joined together and having, therefore, one side in common, just as we represent benzene by a single hexagon.

† These conclusions derive very considerable support from the circumstance that if they are correct, the behaviour of naphthalene is precisely analogous to that of benzene under similar circumstances. Thus it has been pointed out that by the action of various reagents on a large number of mono-substitution derivatives of benzene, *ortho* and *para* di-derivatives are produced to the almost complete exclusion of *meta* derivatives. It will be seen on reference to the figure on p. 348 that each of the hydrogen atoms in naphthalene marked β is in the meta position relatively to one of the two central carbon atoms common to the two nuclei. The formation of α-derivatives from naphthalene by the action of the halogens, nitric acid and sulphuric acid therefore is in harmony with the results observed in the benzene series, since each of the hydrogen atoms marked α is in the ortho position relatively to one or the other of the two central carbon atoms. The behaviour of the mono-derivatives of naphthalene appears moreover closely to resemble that of the corresponding derivatives of benzene. Thus

(1367) *Action of Chlorine on Naphthalene.*—Naphthalene is far more readily acted upon by chlorine and bromine than is benzene; in the first instance additive compounds are produced, which by the loss of haloid acid are converted into haloid substitution derivatives of naphthalene; in fact, it appears that in all cases the formation of the latter is preceded by that of the former, and that haloid substitution derivatives cannot be formed by the direct displacement of hydrogen by the halogen. Laurent was the first to study the products of the action of chlorine on naphthalene; and although his experiments have recently been submitted to careful revision by Faust and Saame (*Ann. Chem. Pharm.*, clx. 65), our knowledge of the chloronaphthalenes is still most imperfect.

Naphthalene chlorides.—Chlorine unites directly with naphthalene forming two compounds: *naphthalene dichloride*, $C_{10}H_8Cl_2$, and *naphthalene tetrachloride*, $C_{10}H_8Cl_4$. The first of these is an oily liquid of a pale yellow colour obtained when chlorine is passed over naphthalene until it becomes liquid. It may be regarded as a dichloro-derivative of a hydrocarbon, $C_{10}H_{10}$, of the acetenylbenzene or C_nH_{2n-10} series. As yet it has not been obtained in a pure state. *Naphthalene tetrachloride* is formed when chlorine is passed into pure fused naphthalene until the mass becomes semi-solid on cooling. When the product is treated with petroleum naphtha a crystalline residue is left which may be readily purified by crystallization from chloroform. It is thus obtained in large rhombic crystals which melt at 182° (359°·6 F.) and are but sparingly soluble in alcohol or ether (Faust and Saame). An isomeric modification appears also to be formed, which is very soluble in alcohol and still more so in ether.

Monochloronaphthalene: $C_{10}H_7Cl$.—The α-derivative, which is formed by heating naphthalene dichloride, $C_{10}H_8Cl_2$, with an alcoholic solution of potassic hydrate, is a colourless oil of high refracting power, boiling at about 252° (485°·6 F.), of the specific gravity of 1·5025—1·5028. It possesses an odour closely resembling that of naphthalene, and is miscible with ether in all propor-

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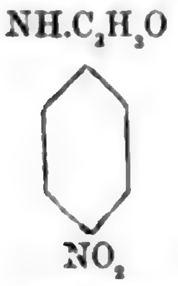
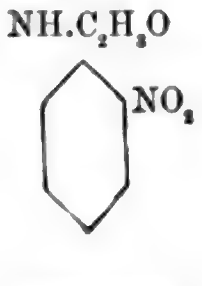
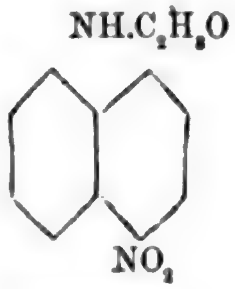
by the action of nitric acid on acetanilide, $C_6H_5.NH(C_2H_3O)$, a mixture of *paranitro*acetanilide, which is the chief product, and *orthonitro*acetanilide is obtained. Similarly, when acenaphthalide is treated with nitric acid, there is reason to believe, as above pointed out, that the nitroacenaphthalide which is the main product is formed by the displacement of a hydrogen atom in the *para*-position relatively to the $NH.C_2H_3O$ group, and there is little doubt that the NO_2 group in the accessory product is in the *ortho*-position relatively to the $NH.C_2H_3O$ group:



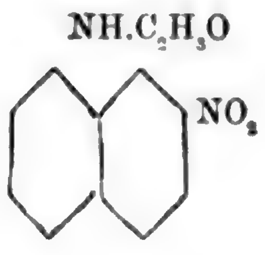
Paranitroacetanilide.



Orthonitroacetanilide.



Paranitro-α-acenaphthalide.



Orthonitro-α-acenaphthalide.

Also when acetanilide is submitted to the action of bromine it is converted into *parabrom*acetanilide, and from Rother's experiments (*Deut. chem. Ges. Ber.*, iv. 850) it appears that when acenaphthalide is similarly treated, the bromine takes up the *para-* position relatively to the $NH.C_2H_3O$ group, since by displacing the latter in the product by hydrogen, ordinary or α-bromonaphthalene is produced (see also Naphtol).

tions. On nitration it is converted into a dinitro-*a*-chloronaphthalene which melts at about 105° (221° F.) (Faust and Saame).

By the action of chlorine on fused nitronaphthalene, the additive compound $C_{10}H_7.NO_2.Cl_2$ is obtained (Atterberg, *Deut. chem. Ges. Ber.*, ix. 316); this is decomposed when heated, furnishing a mixture of chlorinated naphthalenes which appear to be isomeric with those formed from naphthalene. The monochloronaphthalene produced boils at about 255° (491° F.) and has the specific gravity 1·2078; on nitration it yields a dinitro-derivative which melts at 180° (356° F.). This modification is doubtless the β-monochloro-derivative of naphthalene. On distilling nitronaphthalene with phosphoric pentachloride a chloronaphthalene is produced which also is probably the β-modification (De Koninck and Marquart, *ibid.* v. 11. *See* β-bromonaphthalene).

Dichloronaphthalenes: $C_{10}H_6Cl_2$.—Laurent described seven modifications of this compound, but subsequent investigators have only succeeded in obtaining two directly from naphthalene. The dichloronaphthalene produced by the action of a boiling alcoholic solution of potassic hydrate on pure naphthalene tetrachloride forms a crystalline mass, fusing at 36° (96°·8 F.) and boiling at 282° (539°·6 F.). An isomeric body which crystallizes in colourless prisms melting at 68° (154°·4 F.), but also boils at 282° (539°·6 F.), is obtained by fractioning the chloronaphthalenes remaining in solution in the petroleum used to purify the naphthalene tetrachloride as above described. The portion boiling at 280°—285° (536°—545° F.) partly solidifies on standing, and the crystals are purified by pressure and crystallization from a mixture of ether and alcohol. A third dichloronaphthalene, which melts at 107° (224°·6 F.), was obtained by Atterberg from nitronaphthalene.

Like naphthalene itself, the chloro- and dichloronaphthalenes are capable of uniting directly with four atoms of chlorine to form crystalline compounds which are but slightly soluble in alcohol, more readily in ether. *Monochloronaphthalene tetrachloride:* $C_{10}H_7Cl_5$, melts at 130° (266° F.), and when boiled with an alcoholic solution of potassic hydrate, yields *trichloronaphthalene*, $C_{10}H_5Cl_3$. This crystallizes from ether-alcohol in brilliant prisms, melting at 81° (177°·8 F.) An isomeric trichloronaphthalene, melting at 103° (217°·4 F.) is obtained from nitronaphthalene.

Two modifications of *tetrachloronaphthalene:* $C_{10}H_4Cl_4$, are known, one of which is obtained by boiling trichloronaphthalene tetrachloride, $C_{10}H_6Cl_6$, with an alcoholic solution of potassic hydrate. It forms soft colourless needles, melting at 130° (266° F.). According to Atterberg, an isomeric body, melting at 194° (381°·2 F.), is among the products of the action of chlorine on nitronaphthalene.

Pentachloronaphthalene: $C_{10}H_3Cl_5$, has not been prepared directly from naphthalene, but is produced on heating dichloronaphthaquinone with phosphoric pentachloride in a sealed tube at 200° (392° F.):

$$\underset{\text{Dichloronaphthaquinone.}}{C_{10}H_4Cl_2O_2} + 2PCl_5 = \underset{\text{Pentachloronaphthalene.}}{C_{10}H_3Cl_5} + 2POCl_3 + HCl.$$

It forms colourless needles, which are easily soluble in ether, and melt at 108° (226°·4 F.)

Perchloronaphthalene: $C_{10}Cl_8$, is obtained, according to Berthelot and Jungfleisch (*Ann. Chim. Phys.* [4], xv. 332), by treating naphthalene with excess of chlorine in the presence of antimonic perchloride. It crystallizes from carbonic bisulphide in brilliant rhombic prisms, which melt at 135° (275° F.), and boil at 403° (757°·4 F.). According to Faust and Saame, the end product of the action of chlorine on the heated chloronaphthalenes is a compound of the formula $C_{20}H_7Cl_9$, which they term *enneachlorodinaphthalene.* By repeated recrystallization from alcohol it may be obtained in soft white needles, melting at about 157° (314°·6 F.). This body is probably a kind of double salt, as it were, formed by the union of equal numbers of molecules of tetra- and pentachloronaphthalene. Several similar compounds were obtained by Faust and Saame, viz.: the compound $C_{20}H_9Cl_7$, and two isomeric tetrachlorotribromodinaphthalenes, $C_{20}H_9Cl_4Br_3$, these last being the products of the action of bromine on the two isomeric dichloronaphthalenes.

(1368) BROMONAPHTHALENES.—Additive compounds with bromine, corresponding to naphthalene dichloride, $C_{10}H_8Cl_2$, and tetrachloride, $C_{10}H_8Cl_4$, have not been isolated; they appear to be so unstable that they are at once resolved into bromo-substitution derivatives and hydrobromic acid. The compound $C_{10}H_6Br_6$, however, is always the end product of the action of an excess of bromine on naphthalene at the ordinary atmospheric temperature. It crystallizes in large rhombic prisms, and on heating is resolved into tetrabromonaphthalene and hydrobromic acid.

a-Monobromonaphthalene: $C_{10}H_7Br$.—The action of bromine on naphthalene is extremely violent, and in preparing the mono-bromo-derivative it is therefore advisable to dissolve the naphthalene in carbonic bisulphide and then gradually to add the calculated amount of bromine. It is a colourless liquid boiling at 285° (545° F.), of the sp. gr. 1·555 (Glaser, *Ann. Chem. Pharm.*, cxxxv. 40).

β-Bromonaphthalene is obtained by Griess's reaction from β-naphthylamine; it crystallizes in white plates, which melt at 68° (154°·4 F.). *β-chloronaphthalene*, which is also crystalline, and melts at 61° (141°·8 F.), is obtained in a similar manner (Palm, *Deut. chem. Ges. Ber.*, ix. 499). The substance obtained by Atterberg was, therefore, probably impure β-chloronaphthalene.

By gradually mixing bromine with naphthalene in the proportion indicated by the equation: $C_{10}H_8 + 2Br_2 = C_{10}H_6Br_2 + 2HBr$, and crystallizing the product from alcohol, a *dibromonaphthalene* is obtained in long silky needles, which melt at 81° (177°·8 F.); a small quantity of an isomeride is also formed, which melts at 76° (168°·8 F.) (Glaser). Two other isomeric modifications, melting respectively at 126° (258°·8 F.) and 77° (170°·6 F.), are obtained by the action of bromine on naphthalene-α-sulphonic acid (Darmstädter and Wichelham, *Ann Chem. Pharm.*, clii. 304).

Tribromonaphthalene, $C_{10}H_5Br_3$, crystallizes in needles melting at 75° (167° F.) and *tetrabromonaphthalene*, $C_{10}H_4Br_4$, forms stellate groups of slender needles. A *pentabromonaphthalene*, $C_{10}H_3Br_5$, is also known.

Besides these chlorine and bromine derivatives, many compounds are known, containing both bromine and chlorine, but our knowledge of the methods of preparing them in a pure state, and of their properties, is very imperfect.

(1369) *Moniodonaphthalene*, $C_{10}H_7I$, is a colourless liquid formed by the action of excess of iodine on mercuric naphthalide, $C_{20}H_{14}Hg$, or $(C_{10}H_7)_2Hg$.

(1370) NITRONAPHTHALENES.—Naphthalene readily furnishes nitro-derivatives. These compounds have recently been very carefully studied by De Aguiar (*Deut. chem. Ges. Ber.*, v. 370, 897).

a-Mononitronaphthalene: $C_{10}H_7(NO_2)$, is formed by the action of nitric acid on naphthalene in the cold, but may be prepared more conveniently by dissolving naphthalene in glacial acetic acid, then adding ordinary concentrated nitric acid and boiling for half an hour (Aguiar). The crystals which separate on cooling, may be rendered quite pure by recrystallization from alcohol. It forms pale yellow needles which melt at 61° (169°·2 F.), and are easily soluble in carbonic bisulphide.

On boiling naphthalene with fuming nitric acid for some hours, and allowing the solution to cool, a crystalline mass is obtained, consisting of a mixture of about equal quantities of a- and β-dinitronaphthalene. This, when treated successively with small quantities of glacial acetic acid, leaves *a-dinitronaphthalene*, $C_{10}H_6(NO_2)_2$, which, after crystallization from a fresh quantity of the acid, forms hexagonal needles, melting at 216° (420°·8 F.) The more soluble *β-dinitronaphthalene*, $C_{10}H_6(NO_2)_2$, is obtained from the original acetic acid solution by fractional crystallization, in large rhomboidal tables, which melt at 170° (338° F.). By converting acenaphthalide into dinitroacenaphthalide, $C_{10}H_5(NO_2)_2.NH(C_2H_3O)$, and submitting the dinitronaphthylamine, $C_{10}H_5(NO_2)_2.NH_2$, obtained from the latter, to the action of ethylic nitrite, a third dinitronaphthalene is obtained, which crystallizes from alcohol in yellowish needles, melting at 144° (291°·2 F.) (Liebermann and Hammerschlag, *ibid.* ix. 333).

Trinitronaphthalene: $C_{10}H_5(NO_2)_3$.—On heating *a*-dinitronaphthalene for some hours with nitric acid to about 125° (257° F.) in closed tubes, and adding water to the liquid, a precipitate is produced, from which *a-trinitronaphthalene* may be obtained by fractional crystallization from chloroform; it forms monoclinic crystals, readily soluble in chloroform, alcohol, and acetic acid, which melt at 122° (251°·6 F.). A slightly soluble *β-trinitronaphthalene* may be easily prepared from *β*-dinitronaphthalene by adding 5 parts of sulphuric acid to a mixture of 5 parts of fuming nitric acid with one of the dinitro-compound and crystallizing from glacial acetic acid. It forms pale yellow rhombic plates, which melt at 218° (424°·4 F.). When *a*-dinitronaphthalene, however, is treated in this manner, it yields a third modification: *γ-trinitronaphthalene*, which crystallizes from nitric acid in bright yellow scales, melting at 154° (309°·2 F.) (Aguiar; Beilstein and Kuhlberg, *ibid.* vi. 647).

By boiling *a*- or *β*-dinitronaphthalene for a few minutes with 20 parts of a mixture of equal weights of fuming sulphuric and nitric acids, or by long continued heating with nitric acid, they are converted into *a*- and *β-tetranitronaphthalene:* $C_{10}H_4(NO_2)_4$, respectively. The *a*-derivative is almost insoluble in alcohol, but may be crystallized from chloroform. It melts at 259° (498°·2 F.), and detonates violently when heated. The crystalline form belongs to the prismatic system. The *β*-compound crystallizes in long fibrous needles, melting at 200° (392° F.).

(1371) CYANONAPHTHALENES.—*a-Monocyanonaphthalene, a-naphthylic cyanide*, or *a-naphthonitrile*: $C_{10}H_7.CN$, is obtained by distilling potassic naphthalene-*a*-sulphonate with potassic cyanide:

$$C_{10}H_7.KSO_3 \quad + \quad KCN \quad = \quad C_{10}H_7.CN \quad + \quad K_2SO_3.$$

It is also produced by boiling naphthylformamide, $NH.C_{10}H_7.COH$, with concentrated hydrochloric acid, and by heating sulphocarbonaphthalide with finely divided copper. It has an odour resembling that of bitter almond oil, and crystallizes from light petroleum in groups of broad lustrous needles. It melts at 37°·5 (99°·5 F.), and boils at 298° (568°·4 F.). The *β-cyanonaphthalene*, obtained by a similar process from the naphthalene-*β*-sulphonate, crystallizes with difficulty in colourless scales, which melt at 66°·5 (151°·7 F.); it boils at 305° (581° F.). It has but a faint odour, and is less soluble in alcohol than the *a* compound (Merz and Müihauser, *Zeits. Chem.* [2], v. 70; Welkov, *Deut. chem. Ges. Ber.*, ii. 407; Weith, *ibid.* vi. 967).

Dicyanonaphthalenes have been prepared by distilling mixtures of potassic cyanide and the potassic salts of bromonaphthalene- *a*- and *β*-sulphonic acids and the naphthalenedisulphonic acids, but little is known of them (Darmstädter and Wichelhaus, *Ann. Chem. Pharm.*, clii. 307).

(1372) HOMOLOGUES OF NAPHTHALENE.—*Methylnaphthalene:* $C_{11}H_{10}$ or $C_{10}H_7.CH_3$, is a colourless liquid boiling at about 232° (449°·6 F.), and having a density of 1·027 at 11°·5 (52°·7 F.). It is prepared by the action of sodium on a cooled solution of monobromonaphthalene and methylic iodide in ether.

Ethylnaphthalene: $C_{12}H_{12}$ or $C_{10}H_7.C_2H_5$, produced in a similar manner from bromonaphthalene and ethylic bromide, is likewise a colourless liquid. It boils at about 250° (482° F.) (Fittig and Remsen, *Ann. Chem. Pharm.*, clv. 112). Characteristic derivatives of these hydrocarbons have not yet been obtained.

Hexahydroanthracene: $C_{14}H_{16}$—This hydrocarbon is formed on heating dihydroanthracene for ten hours with fuming hydriodic acid and amorphous phosphorus in closed tubes at a temperature of about 200° (392° F.). It crystallizes in colourless laminæ, which are easily soluble in alcohol, ether, and benzene, and which melt at 63° (145°·4 F.). It boils at 290° (554° F.), and at a red heat is resolved into hydrogen and anthracene (Græbe and Liebermann, *Ann. Chem. Pharm.*, Sup. vii. 272).

§ IX. HYDROCARBONS OF THE C_nH_{2n-14} OR DIPHENYL SERIES.

The ninth or C_nH_{2n-14} series of isologous hydrocarbons may be called the diphenyl series from the name of one of its lowest members, although it includes compounds having but a very distant relation to diphenyl. The following is a list of those at present known:

			M.P. °C.	Approximate B.P. °C.
$C_{12}H_{10}$	Acenaphthene	$C_{10}H_6<\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix}$	95°	268°
	Diphenyl	$C_6H_5.C_6H_5$	70°·5	254°
$C_{13}H_{12}$	Diphenylmethane . . .	$CH_2(C_6H_5)_2$	26°	262°
$C_{14}H_{14}$	Tetrahydrophenanthrene.	—	0°	310°
	Paraditolyl	$CH_3.C_6H_4.C_6H_4.CH_3$	121°	280°
	Orthoditolyl	$CH_3.C_6H_4.C_6H_4.CH_3$	liquid	275°
	α-Diphenylethane . . .	$C_6H_5.CH_2.CH_2.C_6H_5$	52°	284°
	β-Diphenylethane . . .	$CH_3.CH(C_6H_5)_2$	below 0°	270°
	Parabenzyltoluene . . .	$CH_3.C_6H_4.CH_2.C_6H_5$	liquid	280°
	Orthobenzyltoluene . .	$CH_3.C_6H_4.CH_2.C_6H_5$	"	280°
$C_{15}H_{16}$	Benzylmetaxylene . . .	$C_6H_5.CH_2.C_6H_3(CH_3)_2$	"	296°
	Benzylparaxylene . . .	$C_6H_5.CH_2.C_6H_3(CH_3)_2$	"	294°
	Benzylethylbenzene . .	$C_6H_5.CH_2.C_6H_4.C_2H_5$	"	295°
	Ditolylmethane	$CH_2(C_6H_4.CH_3)_2$	"	290°
	Dibenzylmethane . . .	$CH_2(CH_2.C_6H_5)_2$	"	290°—300°
	Methyl-β-diphenylethane.	$C_6H_5.CH(CH_3).C_6H_4.CH_3$	"	270°
$C_{16}H_{18}$	Diphenyldimethylethane .	$C_6H_5.CH(CH_3).CH(CH_3).C_6H_5$	124°	—
	Ethyl-β-diphenylethane .	$C_6H_5.CH(CH_3).C_6H_4.C_2H_5$	liquid	—
	α-Ditolylethane	$CH_3.C_6H_4.CH_2.CH_2.C_6H_4.CH_3$	"	297°
	β-Ditolylethane	$CH_3.CH(C_6H_4.CH_3)_2$	"	296°
$C_{19}H_{24}$	Dimesitylmethane . . .	$CH_2\begin{cases}C_6H_2(CH_3)_3\\ C_6H_2(CH_3)_3\end{cases}$	132°	—

None of these hydrocarbons, with the exception of acenaphthene, yield well-defined additive compounds with bromine, but they may readily be converted into substitution derivatives by treatment with that reagent or with nitric acid.

(1373) DIPHENYL OR PHENYLBENZENE; *Phenyl:* $C_{12}H_{10}$ or $C_6H_5.C_6H_5 = 154$.—This hydrocarbon is formed in a variety of reactions, but it is prepared either by Fittig's process, by the action of sodium on a solution of bromobenzene in benzene:*

$$2C_6H_5Br + 2Na = C_{12}H_{10} + 2NaBr;$$

or by taking advantage of the discovery of Berthelot that it is formed by the decomposition of benzene at a red heat.

By the latter method Schultz and Lüddens have prepared considerable quantities of diphenyl, benzene yielding as much as 35 per cent. of its weight in successful operations, according to the former observer. An iron tube (a gun barrel) filled in the middle with pieces of pumice, is heated to bright redness in an ordinary gas combustion furnace (Lüddens), or charcoal furnace (Schultz); it is connected at the one end with a flask containing benzene, and at the other with a condensing apparatus. On boiling the benzene in the flask, its vapour is caused to pass through the red-hot tube; and about 100 to 200 grams may thus be distilled through the tube in the hour. According to Lüddens, however, it is advantageous to dilute the benzene vapour with carbonic anhydride, by passing a current of the latter into the boiling benzene. The unattacked benzene is distilled off the product which collects in the receiver on the water bath, the residue distilled in a current of steam, and crystallized from alcohol. Watson Smith states that the yield of diphenyl is much increased by passing the vapour of benzene mixed with antimonious chloride, $SbCl_3$, through a red-hot tube.

Diphenyl is contained in coal-tar oil, and may be isolated by fractional distillation; it separates from the portion collected at 240°—260° (464°—500° F.) on cooling, and is purified by pressing and crystallization from alcohol (Büchner, *Deut. chem. Ges. Ber.*, viii. 22).

Diphenyl crystallizes from alcohol in thin iridescent plates, which possess a characteristic pleasant odour; it melts at 70°·5 (158°·9 F.) and boils at 254° (489°·2 F.). It is not affected by heating to 250° (482° F.) with hydriodic acid solution (b.p. 127° C.) and phosphorus (Schultz); but according to Berthelot it is converted into hexane when heated with a large excess of a saturated hydriodic acid solution at 280° (536° F.). It is oxidized by a solution of chromic anhydride in glacial acetic acid, benzoic acid being formed (Schultz).

(1374) *Substitution derivatives of Diphenyl.*—The derivatives of diphenyl have been studied by Fittig (*Ann. Chem. Pharm.*, cxxiv. 275; cxxxii. 204; Schultz, *ibid.* clxxiv. 201; Doebner, *ibid.* clxxii. 109; Engelhardt and Latschinoff, *Zeits. Chem.* [2], vii. 259; Osten, *Deut. chem. Ges. Ber.*, vii. 170; Lüddens, *ibid.* viii. 870; Doebner, *ibid.* ix. 129). Chiefly mono- and di-derivatives have been prepared, of which the following is a list:

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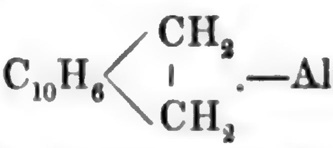
* A certain quantity of by-products is always obtained, consisting of a brominated oil and a crystalline hydrocarbon of the formula $C_{18}H_{12}$ (Schultz).

Name.	Formula.	Melting Point (° Cent.)
Parabromodiphenyl	$C_6H_4Br.C_6H_5$	89°
Parachlorodiphenyl	$C_6H_4Cl.C_6H_5$	75°
Diparabromodiphenyl	$C_6H_4Br.C_6H_4Br$	164°
Diparachlorodiphenyl	$C_6H_4Cl.C_6H_4Cl$	148°
Parametadichlorodiphenyl	$C_6H_3Cl_2.C_6H_5$	179°
Paracyanodiphenyl	$C_6H_4(CN).C_6H_5$	85°
Parametacyanodiphenyl	$C_6H_3(CN)_2.C_6H_5$	234°
Paranitrodiphenyl	$C_6H_4(NO_2).C_6H_5$	113°
Orthonitrodiphenyl (?)	$C_6H_4(NO_2).C_6H_5$	37°
Diparanitrodiphenyl	$C_6H_4(NO_2).C_6H_4(NO_2)$	233°
Orthoparadinitrodiphenyl (?)	$C_6H_3(NO_2)_2.C_6H_5$	93°·5
Parabromoparanitrodiphenyl	$C_6H_4Br.C_6H_4(NO_2)$	173°
Parabromorthonitrodiphenyl (?)	$C_6H_3Br(NO_2).C_6H_5$	65°
Diorthonitrodiparabromodiphenyl (?)	$C_6H_3Br(NO_2).C_6H_3Br(NO_2)$	148°

The main, if not the sole product of the action of bromine, nitric acid, and sulphuric acid on diphenyl, is always a *para*-mono-derivative; that is to say, the radicle displaces an atom of hydrogen in the one C_6H_5 group which is in the para-position relatively to the other C_6H_5 group; only in the case of nitric acid is a small quantity of an isomeric (probably) ortho-mono-derivative obtained. This is proved in the case of the bromo- and nitro-derivatives by their conversion into parabromo- and paranitrobenzoic acid on oxidation; and that the sulpho-acid, $C_6H_5.C_6H_4(SO_3H)$, formed by the action of sulphuric acid on diphenyl, is a para-derivative is shown by the conversion of the oxydiphenyl, $C_6H_5.C_6H_4(OH)$, produced by fusing it with potassic hydrate, into a chlorodiphenyl (by the action of phosphoric pentachloride) which furnishes parachlorobenzoic acid on oxidation.

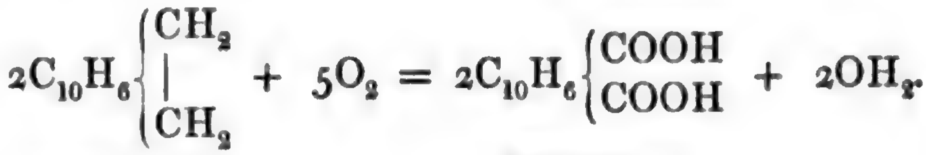
By the further action of bromine and of nitric acid a di-derivative is produced, or at least is the main product, which is formed by the displacement of an atom of hydrogen in the para-position in each of the C_6H_5 groups. Thus, on converting the dinitrodiphenyl, which is the chief product of the action of nitric acid, by partial reduction into amidonitrodiphenyl, and displacing the amido-group in the latter by bromine by Greiss's reaction, a bromonitrodiphenyl is obtained identical with that formed on nitrating parabromodiphenyl, and which furnishes both *parabromo-* and *paranitro*-benzoic acid on oxidation. The dinitrodiphenyl, which is the accessary product, is probably formed by the displacement of two atoms of hydrogen in the same C_6H_5 group, one being in the ortho- and the other in the para-position.

But the action of sulphuric acid offers an exception, for when the disulpho-acid, $C_{12}H_8(SO_3H)_2$, is fused with potassic hydrate, and the resulting dioxydiphenyl is distilled with phosphoric pentachloride, a dichlorodiphenyl, $C_{12}H_8Cl_2$, is obtained, which yields *parameta*dichlorobenzoic acid (m. p. 201° C.) on oxidation; proving that the two sulpho-groups are contained in the same C_6H_5 group.

(1375) **ACENAPHTHENE**: $C_{12}H_{10}$ or  $C_{10}H_6\left\langle\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\right.$.—Although of the same composition as diphenyl, this hydrocarbon is readily distinguished from it and the homologous bodies by its behaviour with bromine and on oxidation, and by forming a compound with trinitrophenol, $C_{12}H_{10}+C_6H_2(NO_2)_3.OH$, crystallizing in orange-yellow needles, which is produced when solutions of equivalent quantities of the two substances in boiling alcohol are mixed.

Acenaphthene was first obtained by Berthelot by passing a mixture of ethylene or acetylene with naphthalene vapour through a red-hot tube, and was subsequently discovered by him in that portion of the heavy coal-tar oil which passes over between 250° and 300° (482° and 572° F.), (*Bull. Soc. Chem.* [2], vii. 275; viii. 245). It is also obtained on passing ethylnaphthalene vapour through a red-hot tube, and by the action of an alcoholic solution of potassic hydrate at 100° (212° F.) on bromethylnaphthalene, $C_{10}H_7.C_2H_4Br$ (Berthelot and Bardy, *Compt. Rend.*, lxxiv. 1463).

According to Behr and Van Dorp (*Ann. Chem. Pharm.*, clxxii. 263) the fraction of coal-oil boiling between 265° and 280° (509° and 536° F.) when allowed to stand in a cold place, deposits acenaphthene in hard flat prisms, which may be purified by crystallization from hot alcohol, in which it is readily soluble; it separates on cooling in brilliant colourless slender prisms, which melt at 95° (203° F.) and boil at 268° (514°·4 F.). On oxidation by potassic dichromate and sulphuric acid mixture it is converted into *naphthalic* acid (Behr and Dorp):



$$2C_{10}H_6\left\{\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right. + 5O_2 = 2C_{10}H_6\left\{\begin{array}{l}COOH\\ COOH\end{array}\right. + 2OH_2.$$

Acenaphthene. Naphthalic acid.

When a molecule of bromine is added to a molecule of acenaphthene dissolved in ether, *bromacenaphthene*, $C_{12}H_9Br$, is produced; it crystallizes from alcohol in plates melting at 52° (125°·6 F.), and is converted into *bromonaphthalic acid* on oxidation. By the action of a larger quantity of bromine on a solution of the hydrocarbon in carbonic bisulphide, *dibromacenaphthene tetrabromide*, $C_{12}H_8Br_6$, is obtained in beautiful white crystals (Blumenthal, *Deut. chem. Ges. Ber.*, vii. 1095). According to Berthelot, a *hexabromide*, $C_{12}H_{10}Br_6$, is formed on adding a slight excess of bromine to a cooled solution of acenaphthene in light petroleum naphtha; it crystallizes from alcohol in slender needles. Since naphthalene combines with at most four atoms of bromine, however, it appears probable that Berthelot's supposed hexabromide is really Blumenthal's dibromotetrabromide.

(1376) HOMOLOGUES OF DIPHENYL. *Formation.*—There are three methods of general application by which hydrocarbons homologous with diphenyl may be produced, viz.: (1) By the action of sodium on the mono-haloid derivatives of the hydrocarbons of the benzene series, both those formed by the displacement of an atom of hydrogen in the C_6 group and in the side chain being available for this purpose:

$$2C_6H_4Br.C_nH_{2n+1} + 2Na = C_6H_4(C_nH_{2n+1}).C_6H_4(C_nH_{2n+1}) + 2NaBr.$$

$$\underset{\text{Bromotoluene.}}{2C_6H_4Br.CH_3} + 2Na = \underset{\text{Ditolyl.}}{C_6H_4(CH_3).C_6H_4(CH_3)} + 2NaBr.$$

By this reaction hydrocarbons strictly homologous with diphenyl are obtained, which is not the case when the reaction takes place in the following manner:

$$2C_6H_5.C_nH_{2n}Cl + 2Na = C_6H_5.C_nH_{2n}.C_nH_{2n}.C_6H_5 + 2NaCl.$$

$$\underset{\text{Benzylic chloride.}}{2C_6H_5.CH_2Cl} + 2Na = \underset{\text{Dibenzyl.}}{C_6H_5.CH_2.CH_2.C_6H_5} + 2NaCl.$$

2. By Zincke's process, by heating a mixture of a hydrocarbon of the benzene series and the monochloro- or monobromo- derivative of a hydrocarbon of the same series containing the halogen in the side chain with finely divided zinc or copper:

$$C_6H_{6-m}(C_nH_{2n+1})_m + C_6H_{5-m}\left\{\begin{matrix} C_nH_{2n}Cl \\ (C_nH_{2n+1})_m \end{matrix}\right. = HCl +$$

$$C_6H_{5-m}\left\{\begin{matrix} C_nH_{2n}.C_6H_{5-m}(C_nH_{2n+1})_m. \\ (C_nH_{2n+1})_m \end{matrix}\right.$$

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} = HCl + \underset{\text{Diphenylmethane.}}{C_6H_5.CH_2.C_6H_5.}$$

$$\underset{\text{Toluene.}}{C_6H_5.CH_3} + \underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} = \underset{\text{Benzyltoluene.}}{C_6H_5.CH_2.C_6H_4.CH_3} + HCl.$$

When zinc is employed, it is only necessary to heat the mixture in an open flask attached to a reversed condenser; with copper, in the case of the lower terms of the benzene series, a higher temperature is required, and the mixture must be heated in sealed tubes; but in the case of the higher terms, the temperature can be raised sufficiently by heating in an open flask. The same action appears to take place, although *far less readily* and completely, when a mixture of the hydrocarbon and haloid derivative is heated. In fact, the metal seems to take no active part in the reaction after it is once started, for if the metal be then removed the action continues with apparently undiminished energy; some metallic chloride, however, is always formed, although the quantity is but small (Zincke, *Ann. Chem. Pharm.*, clix. 367; *Deut. chem. Ges. Ber.*, vi. 137).

3. By Baeyer's method, which is closely allied to Zincke's, concentrated sulphuric acid is caused to act on a mixture of a hydrocarbon of the benzene series with formic or acetic aldehyde;

since, however, formic aldehyde cannot be isolated and acetic aldehyde is rapidly resinified by sulphuric acid, methylenic acetate, $CH_2(C_2H_3O_2)_2$, or methylal, $CH_2(OCH_3)_2$, is employed instead of the former, and its crystalline polymeride, paraldehyde, in place of the latter. It is usually necessary to dilute the mixture with glacial acetic acid before adding the sulphuric acid. Probably, the first action consists in the conversion of the methylal or methylenic acetate, by the sulphuric acid, into the corresponding sulphate, which then enters into reaction with the hydrocarbon:

$$\underset{\text{Methylenic acetate.}}{CH_2\left\{\begin{matrix}C_2H_3O_2\\C_2H_3O_2\end{matrix}\right.} + 2H_2SO_4 = \underset{\text{Methylenic sulphate.}}{CH_2\left\{\begin{matrix}HSO_4\\HSO_4\end{matrix}\right.} + \underset{\text{Acetic acid.}}{2C_2H_4O_2};$$

$$\underset{\text{Methylenic sulphate.}}{CH_2\left\{\begin{matrix}HSO_4\\HSO_4\end{matrix}\right.} + \underset{\text{Benzene.}}{2C_6H_6} = \underset{\text{Diphenylmethane.}}{CH_2\left\{\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right.} + 2H_2SO_4.$$

A similar explanation may be given in the case of acetic aldehyde; the end result, however, is expressed by the equation:

$$CH_3.COH + 2C_6H_{6-m}(C_nH_{2n+1})_m = OH_2 + CH_3.CH\left\{\begin{matrix}C_6H_{5-m}(C_nH_{2n+1})_m\\C_6H_{5-m}(C_nH_{2n+1})_m\end{matrix}\right.$$

By the employment of chlorinated and brominated derivatives of aldehyde, chlorinated and brominated hydrocarbons may be produced; thus:

$$\underset{\text{Chloral.}}{CCl_3.COH} + 2C_6H_6 = \underset{\beta\text{-Diphenyltrichlorethane.}}{CCl_3.CH(C_6H_5)_2} + OH_2.$$

(1377) DIPHENYLMETHANE OR BENZYLBENZENE: $CH_2(C_6H_5)_2 = 168$.— This hydrocarbon is the chief product of the action of zinc on a mixture of benzene and benzylic chloride (see dibenzylbenzene). It is also formed by Baeyer's process from benzene and methylal (*Deut. chem. Ges. Ber.*, vi. 221), and by adding sulphuric acid to an acetic acid solution of benzene and benzylic alcohol (Meyer and Wurster, *ibid.* vi. 963): $C_6H_6 + C_6H_5.CH_2.OH = C_6H_2(C_6H_5)_2 + OH_2$; it is obtained on distilling the baric salt of diphenylacetic acid, $CH(C_6H_5)_2.CO_2H$, with soda-lime (Jena), and according to Staedel (*ibid.* vii. 1480), it is the chief product on heating benzophenone, $CO(C_6H_5)_2$, with zinc powder.

Diphenylmethane crystallizes in colourless monoclinic prisms, which melt at 26° (78°·8 F.); it boils at 262° (503°·6 F.). It possesses an agreeable aromatic odour resembling that of oranges, and is readily soluble in alcohol, ether, and chloroform. On oxidation it is converted into benzophenone, $CO(C_6H_5)_2$. The following nitro-derivatives have been obtained (Doer, *ibid.* v. 795):

	Probable formula.	M.P. ° Cent.
Dinitrodiphenylmethane . . .	$CH_2(C_6H_4.NO_2)_2$	183°
Isodinitrodiphenylmethane . . .	$CH_2\left\{\begin{matrix}C_6H_5\\C_6H_3(NO_2)_2\end{matrix}\right.$	173°
Tetranitrodiphenylmethane . .	$CH_2\left\{\begin{matrix}C_6H_3(NO_2)_2\\C_6H_3(NO_2)_2\end{matrix}\right.$	172°

A crystalline *diphenylchloromethane*, $CHCl(C_6H_5)_2$, which melts at 14° (57°·2 F.), is formed on passing dry hydrochloric acid into well cooled diphenylcarbinol or benzhydrol, $CH(C_6H_5)_2.OH$ (Engler and Bethge, *ibid.* vii. 1128). A liquid *diphenyldichloromethane*, $CCl_2(C_6H_5)_2$, which boils at 305° (581° F.), is produced by heating benzophenone with phosphoric pentachloride (Kekulé and Franchimont, *ibid.* v. 908).

(1378) HYDROCARBONS: $C_{14}H_{14} = 182$.—*Tetrahydrophenanthrene*, $C_{14}H_{14}$.—According to Græbe (*ibid.* viii. 1056) this hydrocarbon is formed on heating phenanthrene with hydriodic acid and phosphorus to about 200° (392° F.). It is an oily liquid which boils at about 310° (590° F.) and solidifies below 0° (32° F.).

Paradimethyldiphenyl or *Paraditolyl* ; *a-Ditolyl* : $\left\{\begin{array}{l} C_6H_4.CH_3 \\ C_6H_4.CH_3 \end{array}\right.$, is prepared by the action of sodium on a solution of parabromotoluene, $C_6H_4Br.CH_3$, in petroleum naphtha (Zincke; Longuinine, *ibid.* iv. 396 and 514); it crystallizes in magnificent monoclinic prisms, which melt at 121° (249°·8 F.).

Orthoditolyl is similarly prepared from orthobromotoluene, but it has not yet been obtained quite free from the isomeride; it is an oily liquid which boils at about 275° (527° F.) (Longuinine). The oxidation products of the ditolyls have not as yet been investigated, but in all probability they are converted into *diphenylcarboxylic* acids, $C_6H_4(COOH).C_6H_4(COOH)$.

a-Diphenylethane or Dibenzyl : $C_6H_5.CH_2.CH_2.C_6H_5$.—This hydrocarbon is most conveniently prepared by the action of metallic sodium on benzylic chloride or bromide: $2C_6H_5.CH_2Cl + 2Na = 2NaCl + C_6H_5.CH_2.CH_2.C_6H_5$ (Fittig and Stelling, *Ann. Chem. Pharm.*, cxxxvii. 258). It is also formed by heating stilbene, $C_{14}H_{12}$, with hydriodic acid to 150° (302° F.) (Limpricht and Schwanert, *ibid.* cxlv. 334).

Dibenzyl crystallizes in white monoclinic prisms which melt at 52° (125°·6 F.); it boils at 284° (543°·2 F.). On passing its vapour over heated pumice, a mixture of stilbene and toluene is obtained. It does not readily undergo oxidation, but is converted by the action of an acetic acid solution of chromic anhydride into benzoic acid (Lippert, *Deut. chem. Ges. Ber.*, ix. 14).

Bromine acts readily upon dibenzyl, but the nature of the products is largely dependent upon the conditions under which the action takes place. When dry bromine is added to the hydrocarbon, much heat is evolved, and a series of bodies is produced which are formed by the displacement of hydrogen in the C_2H_4 group (Marquardt, *Ann. Chem. Pharm.*, cli. 362); viz.:

		M.P. ° Cent.
Bromodibenzyl . .	$C_6H_5.CHBr.CH_2.C_6H_5$	liquid.
Dibromodibenzyl . .	$C_6H_5.CHBr.CHBr.C_6H_5$	228°
Tribromodibenzyl (?) .	$C_6H_4Br.CHBr.CHBr.C_6H_5$	207°–211°

The first of these yields stilbene when treated with an alcoholic solution of potassic hydrate; the second is identical with *stilbene dibromide* (p. 367); the third has not been examined.

By adding bromine to dibenzyl suspended in water, Fittig and Stelling obtained a liquid bromodibenzyl, boiling without decomposition above 320° (608° F.); and a crystalline dibromodibenzyl, melting at 115° (239° F.). These compounds are formed by the displacement of hydrogen in the C_6 groups, for according to Lippert, (*loc. cit.*) the pure monobromo-derivative yields the pure di-derivative, when cautiously treated with bromine, and the latter is converted into *para*bromobenzoic acid on oxidation.

Dibenzyl is also capable of combining directly with bromine, a crystalline compound of the formula $C_{14}H_{14}Br_2$ being obtained by adding bromine to a solution of dibenzyl in pure ether (Fittig, *Ann. Chem. Pharm.*, cxxxvii. 271).

By the action of nitric acid, dibenzyl is converted into a mixture of two isomeric dinitro-derivatives, one of which melts at 166° (330°·8 F.), and the other at 74° (165°·2 F.) (Fittig and Stelling). The former yields a large quantity of paranitrobenzoic acid on oxidation, and is thus proved to be a diparanitrodibenzyl, $C_6H_4(NO_2).CH_2.CH_2.C_6H_4(NO_2)$; the latter also furnishes paranitrobenzoic acid, but in much smaller quantity, and is probably an orthoparadinitroderivative of the formula, $C_6H_4(NO_2).CH_2.CH_2.C_6H_4(NO_2)$.

When treated with sulphuric acid, dibenzyl furnishes dibenzyldiparasulphonic acid, $C_6H_4(SO_3H).CH_2.CH_2.C_6H_4(SO_3H)$ (Kade, *Deut. chem. Ges. Ber.*, vi. 953; vii. 239).

β-Diphenylethane: $CH_3.CH(C_6H_5)_2$.—This hydrocarbon is produced by Zincke's process from benzene and bromethylbenzene, $C_6H_5.CHBr.CH_3$ (Radziszewski, *ibid.* vii. 142); by Baeyer's process, from benzene and paraldehyde (*ibid.* vii. 1190); and by the action of sodium amalgam on an alcoholic solution of β-diphenyltrichlorethane or β-diphenyltribromethane (Goldschmidt, *ibid.* vi. 989, 1501). β-Diphenylethane is a colourless oil of pleasant odour, which boils at about 270° (518° F.), and solidifies at a low temperature to a crystalline mass. On oxidation, it yields benzophenone, $CO(C_6H_5)_2$.

The following haloid derivatives of this hydrocarbon have been prepared by Baeyer's process from benzene or chloro- and bromobenzene, and the mono-, di-, and trichlorinated derivatives of aldehyde and tribromaldehyde (*ibid.* v. 1098; vi. 223, 985, 1439; vii. 1180, 1409):

		M.P. ° Cent.
β-Diphenylmonochlorethane	$CH_2Cl.CH(C_6H_5)_2$	liquid
β-Diphenyldichlorethane	$CHCl_2.CH(C_6H_5)_2$	?
β-Diphenyltrichlorethane	$CCl_3.CH(C_6H_5)_2$	64°
β-Diphenyltribromethane	$CBr_3.CH(C_6H_5)_2$	89°
β-Dimonochlorophenyltrichlorethane . .	$CCl_3.CH(C_6H_4Cl)_2$	105°
β-Dimonobromophenyltribromethane . .	$CCl_3.CH(C_6H_4Br)_2$	140°

Para- and *Orthobenzyltoluene:* $CH_3.C_6H_4.CH_2.C_6H_5$.—The main product of the action of benzylic chloride on toluene in presence of metallic zinc is a mixture of variable proportions of these two hydrocarbons, which cannot be separated; it is a colourless liquid of pleasant odour, which boils at 280° (536° F.) (Zincke, *Ann. Chem. Pharm.*, clxi. 93; Plascuda and Zincke, *Deut. chem. Ges. Ber.*, vi. 906). Behr and Dorp (*ibid.* vii. 18), however, have succeeded in preparing *pure* parabenzyltoluene by strongly heating crystalline parabenzoyltoluene or paratolylphenylketone, $C_6H_5.CO.C_6H_4.CH_3$, with zinc dust. It is an oily liquid, which boils at about 280° (536° F.), and does not solidify in a refrigerating mixture of ice and salt; it does not yield a trace of anthracene when its vapour is passed through a red-hot tube. When the benzyltoluene prepared by Zincke's process is submitted to oxidation with potassic dichromate and sulphuric acid, a mixture of the two isomeric ketones, *para* and β-benzoyltoluene, $C_6H_5.CO.C_6H_4.CH_3$, is obtained, which, on further oxidation, furnishes a mixture of *para-* and *β-benzoylbenzoic acids*, $C_6H_5.CO.C_6H_4.COOH$. There is little doubt that the β-acid and ketone and the hydrocarbon from which they are derived, are *ortho*-derivatives (see anthracene), and that the action of benzylic chloride on toluene resembles that of most other reagents, since an *ortho-* and a *para*-derivative are simultaneously produced (p. 336).

Bromine acts violently on the benzyltoluene prepared by Zincke's process, but no definite bromine derivative has, as yet, been obtained. With nitric acid it yields a dinitro-derivative, $C_{14}H_{12}(NO_2)_2$, melting at 137° (278°·6 F.), together with a small quantity of an isomeride, which melts at about 100° (212° F.); much resinoid matter is also formed. The dinitro-derivative of higher melting point is derived from parabenzyltoluene, and is converted into paranitrobenzoic acid on oxidation, so that it is represented by the formula $C_6H_4(NO_2).CH_2\ C_6H_3(NO_2).CH_3$. The isomeric dinitro-derivative is probably formed from the orthobenzyltoluene. A *tetranitrobenzyltoluene*, $C_{14}H_8(NO_2)_4$, is obtained by the action of a mixture of nitric and sulphuric acids (Zincke, *ibid.* v. 683; vii. 986).

HYDROCARBONS: $C_{15}H_{16} = 196$.—*Benzylmeta-* and *benzylpara-xylene*, $C_6H_5.CH_2.C_6H_3(CH_3)_2$, and *benzylethylbenzene*, $C_6H_5.CH_2.C_6H_4.C_2H_5$, are prepared by Zincke's process from benzylic chloride and meta- or paraxylene or ethylbenzene (Walker, *ibid.* v. 686; Zincke, v. 799). They are colourless liquids having a faint aromatic odour, which boil at about 294°—296° (561°·2—564°·8 F.). On oxidation, benzylethylbenzene is converted into parabenzoylbenzoic acid, $C_6H_5.CO.C_6H_4.COOH$: benzylmetaxylene, however, furnishes benzoylisophthalic acid, $C_6H_5.CO.C_6H_3(COOH)_2$.

Ditolylmethane, $CH_2(C_6H_4.CH_3)_2$, is obtained by Baeyer's process from methylal and toluene. It boils at about 290° (554° F.), and is converted into *dimethylbenzophenone*, $CO(C_6H_4.CH_3)_2$, on oxidation, which, on further oxidation, yields *benzophenonedicarboxylic acid*, $CO(C_6H_4.COOH)_2$. A *dibromo*-derivative, $CH_2(C_6H_3Br.CH_3)_2$, melting at 115° (239° F.), and a *dinitro*-derivative, melting at 164° (327°·2 F.), $CH_2(C_6H_3(NO_2)\ CH_3)_2$, are produced by the action of bromine or nitric acid. A *dichloroditolylmethane*, $CH_2(C_6H_4.CH_2Cl)_2$, which crystallizes in white plates, melting at 105° (221° F.), is formed on adding sulphuric acid to a mixture of methylal and benzylic chloride (Weiler, *ibid.* vii. 1181).

Dibenzylmethane, $CH_2(CH_2.C_6H_5)_2$, has been obtained by Græbe (*ibid.* vii. 1623) by heating dibenzylketone, $CO(CH_2.C_6H_5)_2$, with hydriodic acid and amorphous phosphorus to 180° (356° F.).

Methyl-β-diphenylethane, $CH_3.C_6H_4.CH(CH_3).C_6H_5$, is a liquid hydrocarbon, formed by Zincke's method from toluene and bromethylbenzene; it boils at about 279° (534°·2 F.), and is converted into parabenzoylbenzoic acid on oxidation (Bandrowski, *ibid.* vii. 1016).

(1379) HYDROCARBONS: $C_{16}H_{18} = 210$. — *Diphenyldimethylethane*, $C_6H_5.CH(CH_3).CH(CH_3).C_6H_5$, is formed by the action of sodium on chlor- or bromethylbenzene, $CH_3.CHCl.C_6H_5$ (Engler and Bethge, *ibid.* vii. 1127). It crystallizes from ether in colourless needles, melting at 124° (255°·2 F.).

Ethyl-β-diphenylethane, $C_6H_5.CH(CH_3).C_6H_4.C_2H_5$, is the hydrocarbon produced by the action of zinc on a mixture of ethylbenzene and bromethylbenzene (Radziszewski, *ibid.* vii. 140). On oxidation it is converted into parabenzoylbenzoic acid.

α-Ditolylethane or *dixylyl*, $CH_3.C_6H_4.CH_2.CH_2.C_6H_4.CH_3$, is formed by the action of sodium on the chloroxylene, prepared by the action of chlorine on boiling coal-tar xylene; it is an oily liquid which boils at 296° (564°·8 F.) (Vollrath, *Ann. Chem. Pharm.*, cxliv. 263).

β-Ditolylethane, $CH_3.CH(C_6H_4.CH_3)_2$, is formed on adding toluene to a solution of paraldehyde in sulphuric acid. It is liquid, and boils at about 297° (566°·6 F.). *β-Ditolyltrichlorethane*, $CCl_3.CH(C_6H_4.CH_3)_2$, is obtained by substituting chloral for paraldehyde; it forms colourless crystals which melt at 89° (192°·2 F.) (Fischer, *Deut. chem. Ges. Ber.*, vii. 1193).

(1380) HYDROCARBONS: $C_{19}H_{24} = 252$.—*Dimesitylmethane or hexamethyldiphenylmethane*: $CH_2\left\{\begin{matrix}C_6H_2(CH_3)_3\\C_6H_2(CH_3)_3\end{matrix}\right.$, is very readily obtained, according to

Baeyer (*ibid.* v. 1098), by the action of sulphuric acid on a solution of mesitylene and methylenic acetate in acetic acid. It crystallizes from alcohol or ether in large monoclinic prisms which melt at 132° (269°·6 F.).

§ X. HYDROCARBONS OF THE C_nH_{2n-16} OR STILBENE SERIES.

(1381) Fifteen members of this series have been discovered, but, with the exception of stilbene, very little is known about them. The following is a list:

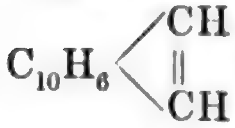
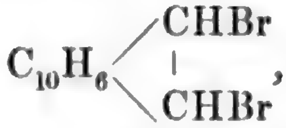
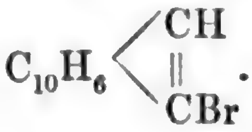
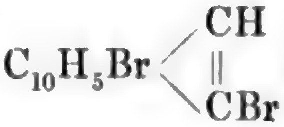
			M.P. ° Cent.	B.P. ° Cent.
$C_{12}H_8$	Acetylenenaphthalene	$C_{10}H_6 < \begin{matrix} CH \\ \Vert \\ CH \end{matrix}$	93°	265°–275°
$C_{13}H_{10}$	Diphenylenemethane or fluorene	$H_2C < \begin{matrix} C_6H_4 \\ \vert \\ C_6H_4 \end{matrix}$	113°	300°–305°
$C_{14}H_{12}$	Dihydroanthracene	—	106°	305°
	α-Diphenylethylene or stilbene	$\begin{matrix} CH.C_6H_5 \\ \Vert \\ CH.C_6H_5 \end{matrix}$	120°	306°
	β-Diphenylethylene or isostilbene	$H_2C{=}C(C_6H_5)_2$	liquid.	277°
$C_{16}H_{16}$	Hexahydropyrene	—	127°	—
	Dicinnamenes	—	—	—
	α-Ditolylethylene or dimethylstilbene	$\begin{matrix} CH.C_6H_4.CH_3 \\ \Vert \\ CH.C_6H_4.CH_3 \end{matrix}$	176°	above 300°
	β-Ditolylethylene	$H_2C{=}C(C_6H_4.CH_3)_2$	liquid.	304°–305°
$C_{18}H_{20}$	Diethylstilbene	$\begin{matrix} CH.C_6H_4.C_2H_5 \\ \Vert \\ CH.C_6H_4.C_2H_5 \end{matrix}$	134°·5	—
	Tetramethylstilbene or α-diparaxylylethylene	$\begin{matrix} CH.C_6H_3(CH_3)_2 \\ \Vert \\ CH.C_6H_3(CH_3)_2 \end{matrix}$	157°	—
	Tetramethylstilbene or α-dimetaxylylethylene	$\begin{matrix} CH.C_6H_3(CH_3)_2 \\ \Vert \\ CH.C_6H_3(CH_3)_2 \end{matrix}$	105°–106°	—
	Tetramethylisostilbene or β-dimetaxylylethylene	$H_2C{=}C \left\{ \begin{matrix} C_6H_3(CH_3)_2 \\ C_6H_3(CH_3)_2 \end{matrix} \right.$	liquid.	335°
$C_{20}H_{24}$	Hexamethylisostilbene or β-dimesitylethylene	$H_2C{=}C \left\{ \begin{matrix} C_6H_2(CH_3)_3 \\ C_6H_2(CH_3)_3 \end{matrix} \right.$	„	—

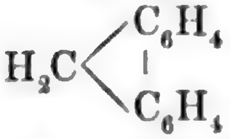
The only general methods for the preparation of hydrocarbons of this series appear to be the passing of the vapour of C_nH_{2n-14} hydrocarbons over heated plumbic oxide:

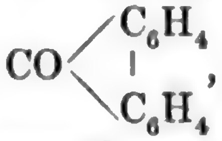
$$\underset{\text{Acenaphthene.}}{C_{12}H_{10}} + PbO = \underset{\text{Acenaphthylene.}}{C_{12}H_8} + OH_2 + Pb;$$

or by the decomposition of their monochlorinated derivatives under the influence of an alkali or of heat:

$$\underset{\beta\text{-Diphenylmonochlorethane.}}{CH_2Cl.CH(C_6H_5)_2} = \underset{\beta\text{-Diphenylethylene.}}{CH_2{=}C(C_6H_5)_2} + HCl.$$

(1382) **Acetylenenaphthalene or Acenaphthylene**: $C_{12}H_8$ or  $C_{10}H_6\left\langle\begin{matrix}CH\\ \|\\ CH\end{matrix}\right.$ = 152.—When acenaphthalene vapour is passed over plumbic oxide, heated nearly to redness, it is almost completely converted into this hydrocarbon (Behr and Dorp, *Ann. Chem. Pharm.*, clxxii. 276; Blumenthal, *Deut. chem. Ges. Ber.*, vii. 1092). Acenaphthylene crystallizes from alcohol, in which it is readily soluble, in large yellow lustrous plates; it melts at about 93° (199°·4 F.), and boils at 265°—275° (509°—527° F.), but is partially decomposed. It furnishes a compound with trinitrophenol difficultly soluble in cold alcohol, and crystallizing in dark yellow needles, which melt at 202° (395°·6 F.). Acenaphthylene is readily reconverted into acenaphthene by treating its alcoholic solution with sodium amalgam; it is converted into naphthalic acid, $C_{10}H_6(COOH)_2$, on oxidation. Acenaphthylene combines with at most two atoms of bromine, forming the compound,  $C_{10}H_6\left\langle\begin{matrix}CHBr\\ |\\ CHBr\end{matrix}\right.$, which crystallizes in white needles melting at 122° (251°·6 F.); this furnishes naphthalic acid on oxidation, and by the action of an alcoholic solution of potassic hydrate, it is converted into *bromacenaphthylene*,  $C_{10}H_6\left\langle\begin{matrix}CH\\ \|\\ CBr\end{matrix}\right.$. By treating this bromacenaphthylene with bromine, the dibromo-derivative,  $C_{10}H_5Br\left\langle\begin{matrix}CH\\ \|\\ CBr\end{matrix}\right.$ is produced.

(1383) **Diphenylenemethane or Fluorene**: $C_{13}H_{10}$ or  $H_2C\left\langle\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right.$ = 166.—Fluorene was discovered by Berthelot in coal-tar, and thus named on account of the beautiful blue fluorescence which it exhibits; it is obtained by crystallizing the fraction boiling between 300° and 305° (572° and 581° F.) from a mixture of alcohol and benzene. Fluorene crystallizes in colourless plates, which melt at 113° (235°·4 F.), and it boils at about 305° (581° F.); it forms a compound with trinitrophenol, $C_{13}H_{10}+C_6H_2(NO_2)_3.OH$, crystallizing from benzene in slender red needles, which melt at about 81° (177°·8 F.). When very carefully treated with bromine, fluorene furnishes a *bromofluorene dibromide*, $C_{13}H_9Br_3$, which crystallizes in fine yellow silky needles;

this is very unstable, and is readily converted into *dibromofluorene*, $C_{13}H_8Br_2$, which crystallizes in large plates melting at 167° (332°·6 F.). On oxidation, fluorene is converted into a *diphenylene-ketone*,  $CO\left\langle\begin{array}{l}C_6H_4\\ \mid\\ C_6H_4\end{array}\right.$, identical with that obtained by Fittig from phenanthrene (Barbier, *Compt. Rend.*, lxxvii. 452; lxxix. 1151; lxxx. 1396).

Diphenylenemethane was obtained by Fittig by distilling diphenyleneketone from phenanthrene with zinc dust, and by Græbe by passing the vapour of diphenylmethane through a red-hot tube; the substances thus prepared are identical, but do not agree in all respects with Barbier's fluorene (Græbe, *Ann. Chem. Pharm.*, clxxiv. 194); probably, however, the difference is due to the presence of small quantities of impurity.

α-DIPHENYLETHYLENE OR STILBENE; *Toluylene:* $C_{14}H_{12}$ or $\begin{array}{l}CH.C_6H_5\\ \|\\ CH.C_6H_5\end{array}$.—This hydrocarbon was first discovered by Laurent in 1843 amongst the products of the dry distillation of thiobenzoic aldehyde, $C_6H_5.CSH$, and from its silky lustre was named stilbene (στίλβω, to shine). It is, however, far more readily prepared by the following methods:

1. By passing dibenzyl or toluene through a red-hot tube, or better over heated plumbic oxide (Dorp, *Deut. chem. Ges. Ber.*, vi. 754; Lorenz, *ibid.* vii. 1096; viii. 1455). The amount of stilbene obtained when toluene and plumbic oxide are employed is equal to about 16 or 18 per cent. of the toluene; diphenyl, ditolyl, phenanthrene and anthracene are also produced at the same time.

2. By distilling benzylic sulphide $(C_6H_5 CH_2)_2S$. Toluene, dibenzyl, benzylic sulphydrate, tolallylic sulphide, $C_{14}H_{10}S$, and thionessal, $C_{28}H_{20}S$, are also formed, and the amount of stilbene produced is equal to about 10 per cent. of the weight of benzylic chloride employed in the preparation of the sulphide (Forst., *Ann. Chem. Pharm.* clxxviii. 370).

3. By the distillation of pure β-diphenylmonochlorethane (p. 362), which splits up sharply into stilbene and hydrochloric acid.

4. By the action of sodium on (o–2) dichlorotoluene (Limpricht); and by distilling a mixture of baric phenylacetate or dibenzyl with sulphur (Radziszewski, *Deut. chem. Ges. Ber.*, vi. 390; viii. 758; Forst., *loc. cit.*); it is also formed in numerous other reactions.

Stilbene crystallizes in colourless nacreous monoclinic plates, which may be obtained of large size by the spontaneous evaporation of an ethereal solution of the hydrocarbon; it melts at 120° (248° F.), and boils at about 306° (582°·8 F.). It is reconverted into dibenzyl, $C_{14}H_{14}$, by heating with concentrated hydriodic acid to 150° (302° F.); on oxidation, it yields benzoic aldehyde and benzoic acid (Zincke, *ibid.* iv. 839):

$$\underset{\text{Stilbene.}}{C_6H_5.CH{=}CH.C_6H_5} + O_2 = \underset{\text{Benzoic aldehyde.}}{2C_6H_5.COH.}$$

Stilbene unites with bromine forming stilbene dibromide (p. 361), $C_6H_5.CHBr.CHBr.C_6H_5$, which crystallizes in small silky needles melting at about 233° (451°·4 F.); when this substance is heated to 130° (266° F.) with an alcoholic solution of potassic hydrate, it is converted into *bromostilbene* (m.p. 25° C.), $C_6H_5.CH{=}CBr.C_6H_5$, which combines with bromine, forming crystalline *tribromodibenzyl* (m.p. about 100° C.), $C_6H_5.CHBr.CBr_2.C_6H_5$.

Nitro-derivatives have not been prepared in a pure state from stilbene, but by the action of an alcoholic solution of potassic hydrate on paranitrobenzylic chloride, $C_6H_4(NO_2).CH_2Cl$, Strakosch has obtained a paradinitrostilbene, $C_{14}H_{10}(NO_2)_2$ (*ibid.* vi. 328). It forms brilliant yellow crystals, which melt above 230° (536° F.).

β-DIPHENYLETHYLENE OR ISOSTILBENE: $H_2C{=}C(C_6H_5)_2$.—This isomeride of stilbene, discovered by Hepp (*ibid.* vii. 1409), is very readily prepared by boiling β-diphenylmonochlorethane (p. 362), $CH_2Cl.CH(C_6H_5)_2$, with an alcoholic solution of potassic hydrate. It is a colourless strongly refracting oil, which boils at 277° (530°·6 F.), and by oxidation yields benzophenone, $CO(C_6H_5)_2$. Its behaviour with bromine is characteristic. In solution in carbonic bisulphide the two unite, doubtless to form β-diphenyldibromethane, $CH_2Br.CBr(C_6H_5)_2$, but after a short time hydrobromic acid is evolved, and β-diphenylmonobromethylene, $CHBr{=}C(C_6H_5)_2$, is obtained. This crystallizes in large prisms, which melt at 50° (122° F.); it does not combine with bromine, and is scarcely affected by oxidizing agents.

A *β-Diphenyldichlorethylene*, $CCl_2{=}C(C_6H_5)_2$, identical with that formed by the action of alkalies on β-diphenyltrichlorethane (p. 362), or by distilling the latter, is obtained by chlorinating well cooled β-diphenylethylene (Hepp); it is a crystalline substance, which melts at 80° (176° F.). An isomeric body, $CH_2{=}C(C_6H_4Cl)_2$, is produced by distilling the β-dimonochlorophenylmonochlorethane, prepared by Baeyer's process from monochloraldehyde and chlorobenzene; it is a colourless oil, boiling at 280°—285° (536°—545° F.) (Hepp). *β-Diphenyldibromethylene*, $CBr_2{=}C(C_6H_5)_2$, obtained by the action of alkalies on β-diphenyltribromethane (p. 362), is a crystalline substance which melts at 83° (181°·4 F.); it does not combine with bromine even when heated with it to 140° (284° F.) (Goldschmidt, *ibid.* vi. 987).

(1384) HYDROCARBONS: $C_{14}H_{12} = 180$.—*Dihydroanthracene:* $C_{14}H_{12}$, is formed by boiling an alcoholic solution of anthracene with sodium amalgam, or by heating anthracene with hydriodic acid solution to 150° (302° F.) for ten hours. It crystallizes in monoclinic plates very similar to naphthalene in appearance, which melt at 106° (222°·8 F.); it boils at 305° (581° F.). Dihydroanthracene is reconverted into anthracene by boiling with sulphuric acid or by passing its vapour through a red-hot tube (Græbe and Liebermann, *Ann. Chem.*

Pharm. Suppl., vii. 265). It is very readily oxidized and converted into anthraquinone, $C_{14}H_8O_2$, and on treatment with bromine it yields dibromanthracene, $C_{14}H_8Br_2$.

(1385) HOMOLOGUES OF STILBENE.—The β-diphenylmonochlorethane prepared by Baeyer's process from monochloraldehyde and benzene (p. 362), it will be remembered, is converted by the action of an alcoholic solution of potassic hydrate into β-diphenylethylene or isostilbene, thus :

$$CH_2Cl.CH(C_6H_5)_2 + KHO = CH_2{=}C(C_6H_5)_2 + KCl + OH_2.$$

In this compound *both* C_6H_5 groups must be supposed to be attached to the *same* carbon atom, since it yields benzophenone, $CO(C_6H_5)_2$, when oxidized. But by splitting off the elements of hydrochloric acid, by submitting the compound to dry distillation instead of to the action of an alkali, α-diphenylethylene or stilbene is formed, so that in this case a remarkable isomeric change takes place, for its behaviour on oxidation shows that the two C_6H_5 groups in stilbene are attached to *different* carbon atoms :

$$CH_2Cl.CH(C_6H_5)_2 = C_6H_5.CH{=}CH.C_6H_5 + HCl.$$

When the homologues of β-diphenylmonochlorethane, prepared from the homologues of benzene and monochloraldehyde, are similarly treated, they furnish a series of homologues of isostilbene, but all do not yield homologues of stilbene. Thus the chlorinated hydrocarbons prepared with the aid of toluene and ethylbenzene are entirely converted into dimethyl- and diethylstilbene on distillation, but paraxylene, $C_6H_4(CH_3)_2$, and monochloraldehyde furnish a chlorinated hydrocarbon, $CH_2Cl.CH\left\{\begin{array}{l}C_6H_3(CH_3)_2\\C_6H_3(CH_3)_2\end{array}\right.$, which yields a mixture of a tetramethylstilbene melting at 157° (314°·6 F.) and a liquid tetramethylisostilbene; the same is the case with that derived from metaxylene. The chlorinated hydrocarbon obtained from mesitylene, however, appears to yield only the isostilbene homologue on distillation; and it has already been pointed out that the chlorinated hydrocarbon from monochloraldehyde and chlorobenzene does not yield a stilbene, but an isostilbene derivative on distillation (Hepp, *loc. cit.*).

The methylated homologues of stilbene all form additive compounds with bromine, and hydrobromic acid is not evolved when they are brought in contact with bromine in carbonic bisulphide solution. When, however, bromine is added to solutions of the homologues of isostilbene in carbonic bisulphide, although at first the bromine enters into union with the hydrocarbons, hydrobromic acid is very soon evolved, and substitution derivatives are obtained.

The homologues of stilbene and isostilbene are also characterized and distinguished by their behaviour on oxidation. Thus dimethylstilbene, $C_6H_4(CH_3).HC{=}CH.C_6H_4(CH_3)$, yields *paratoluic acid*, $C_6H_4(CH_3).COOH$, on oxidation with nitric acid, and *terephthalic acid*, $C_6H_4(COOH)_2$, when submitted to the action of chromic acid mixture; whilst dimethylisostilbene, $H_2C{=}C(C_6H_4.CH_3)_2$, is converted into *ditolylketone*, $CO(C_6H_4.CH_3)_2$. Diethylstilbene also yields terephthalic acid. On oxidizing the tetramethylstilbene prepared with the aid of metaxylene, *xylic acid*, (p. 288) $C_6H_3(CH_3)_2.COOH$ ($COOH : CH_3 : CH_3 = 1 : 2 : 4$) is produced.

Dicinnamene or *Distyrolene*: $C_{16}H_{16}$.—By heating cinnamene, C_8H_8, with hydrochloric acid to 170° (338° F.), it is converted into an oily liquid which is not reconverted into cinnamene on distillation, but unites with bromine to form the compound $C_{16}H_{16}Br_2$ (Erlenmeyer, *Ann. Chem. Pharm.*, cxxxv. 122). A polymeride of cinnamene to which Engler and Leist (*Deut. chem. Ges. Ber.*, vi. 256) assign the formula $C_{16}H_{16}$ is formed in considerable quantity when calcic cinnamate is submitted to destructive distillation. It crystallizes in plates which melt at 117° (242°·6 F.).

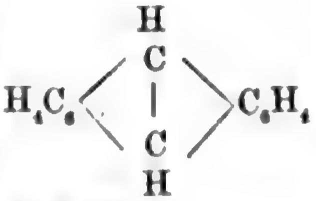
Hexahydropyrene: $C_{16}H_{16}$.—Pyrene is not acted on by sodium amalgam, but when heated with hydriodic acid and amorphous phosphorus to about 200° (392° F.) it takes up hydrogen and is converted into a mixture of hydrides, from which the hydrocarbon $C_{16}H_{16}$ may be extracted by careful fractional crystallization from alcohol. It forms colourless needles or prisms, which melt at 127° (260°·6 F.). At a red heat it is resolved into pyrene and hydrogen (Græbe, *Ann. Chem. Pharm.*, clviii. 285).

APPENDIX TO (1363).—A homologue of phenylacetylene has recently been prepared by Morgan (*Journ. Chem. Soc.*, 1876, vol. i. p. 162) by heating sodium phenylacetylene with ethylic iodide in sealed tubes to 120°—140° (248°—284° F.). *Ethylphenylacetylene*, $C_6H_5.C{\equiv}C.C_2H_5$, is a colourless highly refractive liquid, which boils at about 202° (395°·6 F.); it combines immediately with bromine, and also with hydrobromic acid when heated with a saturated solution for a few hours at 150° (302° F.). In his paper Morgan states that a very poor yield of phenylacetylene is obtained by heating phenyldichlorethane with potassic hydrate, but that a fair amount of the hydrocarbon is produced by distilling it through a glass tube containing soda-lime, and heated a little below redness; this observation is of interest as it serves to explain the discrepancy pointed out in the foot note, p. 344.

APPENDIX TO (1377).—*Methyldiphenyl* or *paratolylphenyl*: $C_6H_5.C_6H_4.CH_3$, the isomeride of diphenylmethane, is the product of the action of sodium on a mixture of bromobenzene and parabromotoluene (Carnelly, *ibid.* p. 13). It is a colourless refractive liquid, which boils at about 265° (509° F.); it becomes solid in a freezing mixture, and melts at about − 2° (28°·4 F.). When oxidized, it is converted into paraphenylbenzoic acid, $C_6H_5.C_6H_4.COOH$. It furnishes two isomeric mononitro-derivatives on nitration.

§ XI. HYDROCARBONS OF THE C_nH_{2n-18} OR ANTHRACENE SERIES.

(1386) The most important member of the series is that which gives it its name—viz., anthracene. At present the series includes the following hydrocarbons:

			M.P. ° C.	B.P. ° C.
$C_{14}H_{10}$	Anthracene		213°	360°
	Phenanthrene . . .	$C_6H_4.CH$ $\vert \quad \Vert$ $C_6H_4.CH$	96°	340°
	Tolane	$C.C_6H_5$ $\vert\vert\vert$ $C.C_6H_5$	60°	—
$C_{15}H_{12}$	Methylanthracene . .	$C_{14}H_9.CH_3$	200°	—
$C_{16}H_{14}$	Dimethyltolane . . .	$C.C_6H_4.CH_3$ $\vert\vert\vert$ $C.C_6H_4.CH_3$	136°	—
	Dimethylanthracene (?)	——	200°	—
$C_{18}H_{18}$	Retene	——	—	—

There are no general methods for the formation of hydrocarbons of this series, but tolane and its homologues may be prepared from stilbene and its homologues by combining them with a molecule of bromine and eliminating hydrobromic acid by acting on the product with an alkaline hydrate; thus:

$$\underset{\text{Stilbene dibromide.}}{C_{14}H_{12}Br_2} = \underset{\text{Tolane.}}{C_{14}H_{10}} + 2HBr.$$

(1387) ANTHRACENE: $C_{14}H_{10}$ = 178.— This hydrocarbon, which was formerly called Paranaphthalene, was discovered in 1832 by Dumas and Laurent amongst the products of the destructive distillation of coal, and was subsequently examined by Laurent, by Fritzsche, and by Anderson; Fritzsche's *photene* being really pure anthracene. Since Græbe and Liebermann's discovery that alizarin was an anthracene derivative, it has attracted the attention of chemists, and has been the subject of numerous and extended investigations.

Anthracene besides being obtained from coal-tar, is formed in a great variety of reactions taking place at high temperatures. Thus it is obtained when a mixture of ethylene with benzene, diphenyl, or chrysene, $C_{18}H_{12}$, or of benzene with cinnamene or naphthalene, is passed through a red-hot tube (Berthelot); anthracene is not the only product of these reactions, however.

When the benzyltoluene prepared by Zincke's method is passed over heated plumbic oxide, it yields anthracene in considerable quantity, but since it cannot be obtained from pure parabenzyltoluene, which is not altered by a red-heat (p. 362), there is no doubt that it is formed from the β- or orthobenzyltoluene which accompanies the former in the product of the action of zinc on a mixture of toluene and benzylic chloride. The liquid or β-tolylphenylketone, formed together with α- or paratolylphenylketone by oxidizing crude benzyltoluene, also furnishes anthracene when passed over heated zinc dust (Behr and Dorp, *Deut. chem. Ges. Ber.*, v. 1070; vi. 754; vii. 16):

$$\underset{\text{Orthobenzyltoluene.}}{C_{14}H_{14}} = \underset{\text{Anthracene.}}{C_{14}H_{10}} + H_2.$$

$$\underset{\text{Orthotolylphenylketone.}}{C_{14}H_{12}O} + Zn = \underset{\text{Anthracene.}}{C_{14}H_{10}} + ZnO + H_2.$$

The formation of anthracene which takes place when toluene is passed through a red-hot tube, or over heated plumbic oxide, is doubtless due to the production of benzyltoluene: $2\,C_7H_8 = C_{14}H_{14} + H_2$, which by further loss of hydrogen is converted into anthracene (Dorp, *ibid.* v. 1072).

When alizarin is distilled with zinc dust, which is a mixture of zinc, zincic oxide, and zincic hydrate, it is converted into anthracene, the necessary hydrogen being probably derived from the zincic hydrate (Græbe and Liebermann, *ibid.* i. 49):

$$\underset{\text{Alizarin.}}{C_{14}H_8O_4} + 4Zn + H_2 = \underset{\text{Anthracene.}}{C_{14}H_{10}} + 4ZnO.$$

Purpurin and the so-called rufigallic and frangulic acids also yield anthracene when thus treated.

Lastly, anthracene is amongst the substances isolated by distillation from the product of the action of zinc on a mixture of toluene and benzylic chloride (Weber and Zincke, *ibid.* vii. 1153), and it is also obtained together with benzyltoluene and substances of very high boiling-point when benzylic chloride is heated with water in sealed tubes to 200° (392° F.), and the product distilled (Limpricht, *Ann. Chem. Pharm.*, cxxix. 303; Dorp, *Deut. chem. Ges. Ber.*, v. 1070; Zincke, *ibid.* vii. 276).

In neither of these cases is anthracene a direct product, but it is formed by the splitting up of more complex hydrocarbons under the influence of heat. When a mixture of toluene and benzylic chloride is heated with zinc, a number of benzyltoluenes are produced (see benzyl- and dibenzyltoluene), one or more $C_6H_5.CH_2$ groups being introduced in place of hydrogen in the C_6H_5 group of toluene. In the formation of these bodies, both the toluene and the benzylic chloride take part, but a second set of hydrocarbons of the composition nC_7H_6 (Zincke, *Ann. Chem. Pharm.*, clix. 368) are formed from the benzylic chloride alone, and are the result of the removal of *n* molecules of hydrochloric acid from *n* molecules of benzylic chloride; these substances, however, are decomposed on distillation, yielding anthracene and other products, and there is reason to believe that anthracene is not present in coal-tar, but that it is in a similar manner formed on distilling the tar by the decomposition of more complex hydrocarbons (Zincke). When benzylic chloride is heated with water, the first action which takes place is that represented by the equation:

$$C_6H_5.CH_2Cl + C_6H_5.CH_2Cl = HCl + C_6H_5.CH_2.C_6H_4.CH_2Cl.$$

The product of this reaction may then either lose HCl, or may react upon another molecule of benzylic chloride, forming the chloride $C_{21}H_{19}Cl$, which in turn may undergo alteration in a similar manner. In this way, hydrocarbons of the composition nC_7H_6, and chlorinated compounds, such as $C_{14}H_{13}Cl$, $C_{21}H_{19}Cl$, $C_{28}H_{25}Cl$, &c., may be produced, and by the action of water on the latter, small quantities of oxygenated bodies are also formed, the molecular weights of the products being greater the longer the heating is continued. The product of the action of water on benzylic chloride is therefore extremely complex: it does not contain benzyltoluene nor anthracene, however; but on submitting it to distillation, water, hydrochloric acid, benzylic chloride, benzyltoluene, and viscid hydrocarbons—which on further heating yield anthracene and toluene—are obtained.

Anthracene is now manufactured on a large scale from the higher boiling portions obtained in the distillation of coal-tar, which when allowed to stand for some time at a low temperature deposit the impure substance in the solid state. It is freed from the liquid portions by means of a centrifugal machine and hydraulic pressure, and purified by repeated treatment with boiling petroleum or light coal oil, or by sublimation in a current of air, or of superheated steam. It still, however, retains small quantities of impurities which may be removed by exposing it to sunshine until colourless, and then boiling it with an alcoholic solution of trinitrophenol or picric acid to remove traces of a more soluble hydrocarbon of higher boiling-point. It should finally be crystallized from boiling alcohol. This method has the disadvantage, however, that by the exposure to light small quantities of paranthracene are produced. Perkin (*private communication*) recommends the following mode of treatment. Crude anthracene is first thoroughly washed with petroleum spirit and dried. It is then distilled with about one-third of its weight of solid potassic hydrate; this combines with the carbazol, and also causes many of the impurities to carbonize. The distilled product is then ground up with several times its bulk of carbonic bisulphide, thrown on a filter, and washed with fresh bisulphide; it is then dried and crystallized two or three times from benzene. The first half of the distillate generally yields the best product to work with, as it is more readily purified than the latter portions.

When quite pure, anthracene crystallizes in colourless, well defined, monoclinic plates, which exhibit a beautiful violet fluorescence. It melts at 213° (415°·4 F.), and distils unchanged at about 360° (680° F.). It is insoluble in water, slightly soluble in alcohol, but more readily in benzene. When it is dissolved together with trinitrophenol in boiling benzene, deep ruby-red crystals of the compound $C_{14}H_{10} + C_6H_2(NO_2)_3.OH$, are formed; this is decomposed into its components by water and alcohol.

Oxidizing agents convert anthracene into *anthraquinone*, $C_{14}H_8O_2$, whilst hydriodic acid produces *dihydroanthracene*, $C_{14}H_{12}$ (1384) and *hexahydroanthracene* $C_{14}H_{16}$ (1372); or at 280° (536° F.), if the acid is very concentrated and in large excess, various members of the paraffin series are obtained, amongst which are tetradecane, heptane, hexane, and ethane, also benzene and toluene (Berthelot).

By the action of nitric acid, anthracene is converted into anthraquinone and nitro-derivatives of the latter, and all attempts to obtain nitro-derivatives of anthracene have been unsuccessful (Schmidt, *Journ. pr. Chem.* [2], ix. 241). By careful treatment with sulphuric acid it may be made to furnish a mixture of two isomeric *anthracenesulphonic acids*, $C_{14}H_9.SO_3H$ (Linke, *ibid.* [2], xi. 222); but there is a great tendency to form viscid carbonized products.

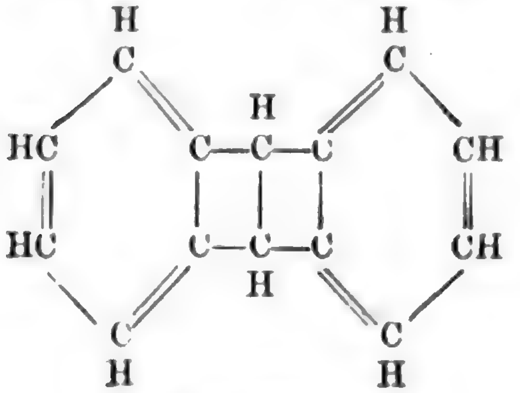
(1388) *Action of Chlorine and Bromine on Anthracene.*—The first action of these halogens on anthracene is to form additive compounds, which, however, are very easily resolved into haloid acid and haloid substitution derivatives; the bromine compounds, in fact, are so unstable that they cannot be isolated. The haloid derivatives combine with the halogens forming comparatively stable bodies, but at most four atoms of halogen unite with a molecule of the haloid derivative.

Anthracene dichloride, $C_{14}H_{10}Cl_2$, is formed when chlorine is slowly passed over anthracene for not too long a time; by heating, or by the action of an alcoholic solution of potassic hydrate, it is converted into *monochloranthracene*,

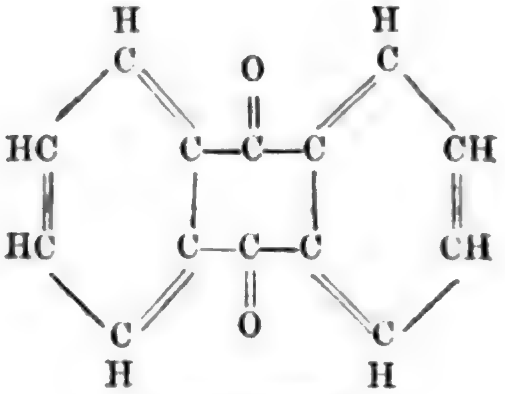
$C_{14}H_9Cl$ (Anderson); little is known of either of these bodies. *Dichloranthracene*, $C_{14}H_8Cl_2$, is prepared by heating the hydrocarbon at 100° (212° F.) in chlorine, or, according to Perkin (*Journ. Chem. Soc.*, xxiv. 14), by passing chlorine over benzene holding in solution about one-fifth of its weight of anthracene until the mass becomes pasty. The crude product is pressed, distilled, and then repeatedly crystallized from benzene. It forms golden-yellow scales which melt at 205° (401° F.), and are sparingly soluble in alcohol or ether, but easily in benzene; on oxidation it yields anthraquinone. *Tetrachloranthracene*, $C_{14}H_6Cl_4$, forms stellate groups of golden-yellow needles, which melt at 220° (428° F.). It is prepared by passing chlorine over anthracene heated to about 180° (356° F.), treating the resulting compound (doubtless dichloranthracene tetrachloride, $C_{10}H_8Cl_6$) with an alcoholic solution of potassic hydrate, and crystallizing the product from benzene. It yields dichloranthraquinone when oxidized (Græbe and Liebermann, *Ann. Chem. Pharm.* Suppl., vii. 283).

Monobromanthracene has not been obtained. When bromine is added to a solution of anthracene in carbonic bisulphide, however small the quantity of bromine taken, dibromanthracene is always produced; more or less anthracene remaining unaltered. *Dibromanthracene*, $C_{14}H_8Br_2$, forms golden-yellow needles, which melt at 221° (429°·8 F.); when it is heated with an alcoholic solution of potassic hydrate to 170° (338° F.) it is reconverted into anthracene; oxidizing agents transform it into anthraquinone. Bromine is without action on dibromanthracene dissolved in carbonic bisulphide, but when the dry substance is placed under a bell jar with an open vessel containing bromine, it is converted into *Dibromanthracene tetrabromide*, $C_{10}H_8Br_6$. This crystallizes in thick colourless plates, slightly soluble in alcohol and ether, more readily in boiling benzene. It melts between 170° and 180° (338° and 356° F.), but is decomposed and converted into *tribromanthracene*, $C_{14}H_7Br_3$, hydrobromic acid and bromine; by heating with an alcoholic solution of potassic hydrate, however, it furnishes *tetrabromanthracene*, $C_{14}H_6Br_4$. Tribromanthracene crystallizes in yellow needles, melting at 169° (336°·2 F.), whilst tetrabromanthracene, which closely resembles it, melts at 254° (489°·2 F.). Tribromanthracene is easily soluble in benzene, which dissolves di- and tetrabromanthracene with difficulty; it forms a tetrabromide with bromine, $C_{10}H_7Br_7$. When oxidized, tribromanthracene yields bromanthraquinone, and tetrabromanthracene is converted into dibromanthraquinone (Græbe and Liebermann, *loc. cit.*, 274–282).

(1389) *Constitution of Anthracene and its Derivatives.*—The following symbol is that which best enables us to represent the formation of anthracene and its behaviour under various circumstances, that of anthraquinone being also given since it is impossible to discuss the constitution of anthracene without considering that of anthraquinone:



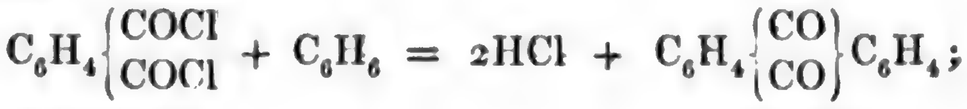
Anthracene.



Anthraquinone.

Anthracene, it will be seen, is represented as formed from two benzene molecules, which are not directly united but are linked together as it were by two atoms of carbon; each of the latter being united to the other by one of its affinities, as well as to an atom of hydrogen, and by the two remaining affinities to each of the C_6 groups. The tetrad C_2H_2 group which thus links together the two C_6 groups is represented as displacing *two* atoms of hydrogen in *each* molecule of benzene which are in the orthoposition relatively to each other, for it will be remembered, anthracene is not obtained from parabenzyltoluene (p. 362), but from the isomeride formed together with it, which there is good reason to believe is *ortho*benzyltoluene. Although, however, its formation from orthobenzyltoluene proves that in the *one* C_6 group two atoms of hydrogen are displaced which are in the ortho-position relatively to each other, it does not in any way necessitate the assumption that this is the case with regard to the second C_6 group, nor is there any evidence at present to prove this; analogy alone leads us to believe that in all probability it is so.

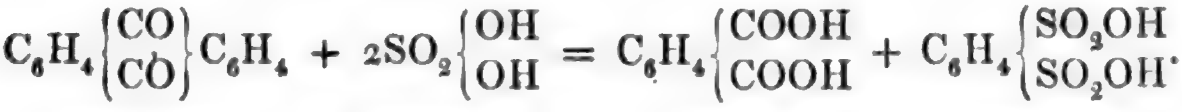
In the conversion of anthracene into anthraquinone, the two atoms of carbon which link together the two C_6 groups become disunited, and each combines by two of its affinities with an atom of oxygen. That these two central atoms of carbon, as they may be termed, are affected, is proved by the formation of anthraquinone when a mixture of phthalic chloride and benzene is heated with metallic zinc (Piccard, *Deut. chem. Ges. Ber.*, vii. 1785):



$$\mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{COCl}\\ \mathrm{COCl}\end{matrix}\right. + \mathrm{C_6H_6} = \mathrm{2HCl} + \mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right\}\mathrm{C_6H_4};$$

Phthalic chloride. Anthraquinone.

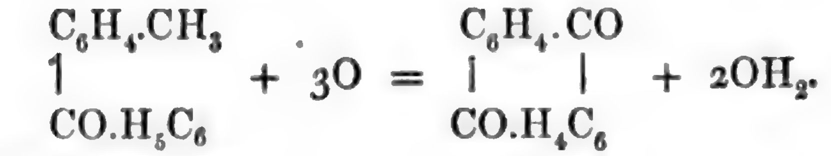
and by the formation of phthalic acid in large quantity when anthraquinone is heated with sulphuric acid to 270° (518° F.), the reaction being probably represented by the equation (Weith and Bindschedler, *ibid.* vii. 1106):



$$\mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right\}\mathrm{C_6H_4} + \mathrm{2SO_2}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. = \mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix}\right. + \mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{SO_2OH}\\ \mathrm{SO_2OH}\end{matrix}\right..$$

Anthraquinone. Sulphuric acid. Phthalic acid. Benzenedisulphonic acid.

Anthraquinone is also obtained when β- or *ortho*tolylphenylketone (orthobenzoyltoluene) is oxidized (Behr and Dorp, *ibid.* vii. 18):



$$\begin{array}{c} C_6H_4.CH_3 \\ | \\ CO.H_5C_6 \end{array} + 3O = \begin{array}{c} C_6H_4.CO \\ | \qquad | \\ CO.H_4C_6 \end{array} + 2OH_2.$$

Orthobenzoyltoluene. Anthraquinone.

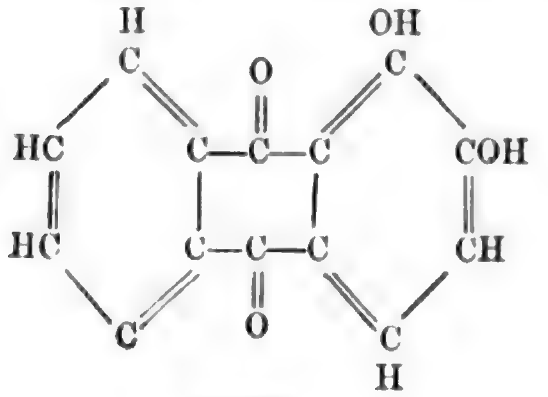
The proof derived from the formation of phthalic acid from anthraquinone, and *vice versâ*, that the two CO groups in anthraquinone are associated in the one C_6 group with contiguous carbon atoms may be regarded also as proof that the benzyltoluene formed together with parabenzyltoluene, and the ketone into which it is converted on oxidation, are really *ortho*-di-derivatives of benzene.

It has been stated above that dichlor- and dibromanthracene furnish anthraquinone on oxidation; it therefore follows that the first action of the halogens on anthracene is to displace the atoms of hydrogen associated with the two central carbon atoms. When tetrachlor- and tetrabromanthracene are oxidized, however, dichlor- and dibromanthraquinone are produced; the latter is also formed by heating anthraquinone with bromine, and when it is fused with potassic hydrate it is converted into *dioxyanthraquinone* or *alizarin*:

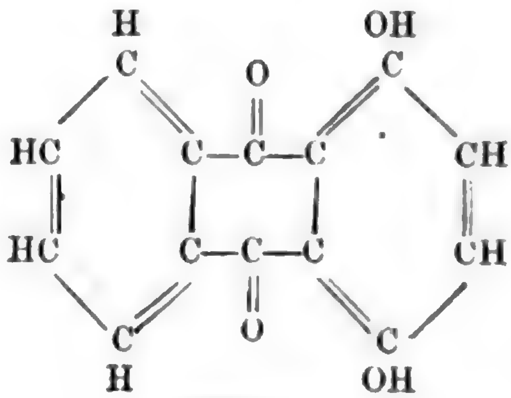
$$C_{14}H_6Br_2O_2 + 2KHO = C_{14}H_6(OH)_2O_2 + 2KBr.$$

Dibromanthraquinone. Alizarin.

Admitting that the two atoms of bromine are directly displaced, and that the CO groups in anthraquinone are associated in both C_6 groups with contiguous carbon atoms, this result enables us also to infer the nature of tetrabromanthracene: for Baeyer and Caro have shown that alizarin is produced by the action of phthalic anhydride on the *ortho*dioxybenzene, *pyrocatechin*, $C_6H_4(OH)_2$, in presence of sulphuric acid, and that in a similar manner *chinizarin*, which is an isomeride of alizarin, may be produced from the *para*dioxybenzene, *hydroquinone* (*ibid.* vii. 972). The only formulæ which can therefore be assigned to chinizarin and alizarin are those represented by the following symbols:



Alizarin.



Chinizarin.

But since the bromine atoms in dibromanthraquinone occupy the same position as the OH groups in alizarin it follows that two of the bromine atoms in tetrabromanthracene displace hydrogen atoms attached to the two central carbon atoms, whilst the remaining two displace hydrogen atoms in the ortho-position relatively to each other in one of the C_6 groups.

(1390) PARANTHRACENE: $C_{14}H_{10}$.—Fritzsche discovered that light has a most remarkable influence upon anthracene. When a cold saturated solution in benzene is exposed to sunlight, small microscopic plates crystallize out, which have the same composition as anthracene, but very different properties. Paranthracene is not only very sparingly soluble, but melts at 244° (471°·2 F.), or 30° higher than anthracene; it is reconverted into anthracene when fused, however. It crystallizes in small prismatic crystals, very different from the plates in which anthracene is obtained. It does not combine with trinitrophenol, neither is it attacked by bromine nor boiling concentrated nitric acid; but by the action of warm fuming nitric acid it is converted into anthraquinone. It also furnishes anthraquinone on oxidation by chromic acid (Schmidt, *Journ. pr. Chem.* [2], ix. 247).

(1391) PHENANTHRENE: $C_{14}H_{10}$.—This hydrocarbon is isomeric with anthracene, and, like it, is found in the higher boiling portions of coal oil. It was discovered by Glaser (*Deut. chem. Ges. Ber.*, v. 861) in crude anthracene, and subsequently examined by Græbe (*Ann. Chem. Pharm.*, clxvii. 131), whilst it was observed almost at the same time by Ostermayer and Fittig (*Deut. chem. Ges. Ber.*, v. 933, and *Ann. Chem. Pharm.*, clxvi. 361).

Phenanthrene not only exists in coal tar, but has also been formed synthetically by passing the vapour of stilbene through a red-hot tube (Græbe): $C_{14}H_{12}=C_{14}H_{10}+H_2$; very little hydrogen is evolved, however, but by its action on a portion of the stilbene toluene is produced: $C_{14}H_{12}+2H_2=2C_7H_8$. In like manner, when the vapour of dibenzyl, $C_{14}H_{14}$, is heated to redness, stilbene is first formed, and in part converted into phenanthrene; and it may even be produced in this way from toluene (p. 366), which doubtless furnishes in succession dibenzyl and stilbene before it yields phenanthrene. According to Barbier (*Deut. chem. Ges. Ber.*, vii. 1444), when a mixture of diphenyl and ethylene, or of benzene and cinnamene is heated to redness, phenanthrene is produced.

Phenanthrene may be prepared from crude anthracene by distilling it and collecting apart the portion which comes over between 310° and 350° (608° and 662° F.). Repeated crystallizations from alcohol, rejecting the less soluble portions, suffice to purify it (Ostermayer, *ibid.* vii. 1090); or, as suggested by Schmidt (*ibid.* vii. 205), it may be dissolved in hot alcohol of 85 per cent., and treated with nitric acid, whereby the anthracene is converted into anthraquinone and dinitroanthraquinone, which form a resinous cake, whilst the clear solution solidifies on cooling to a mass of crystals of phenanthrene. This may be readily purified by crystallizing it from dilute alcohol. The crude material may also be purified by dissolving it in hot coal-oil boiling at 100°—140° (212°—284° F.), together with 1⅓ times its weight of trinitrophenol or picric acid (Græbe). On cooling, the compound with trinitrophenol, $C_{14}H_{10} + C_6H_2(NO_2)_3OH$ is deposited in long yellow needles, melting at 145° (293° F.); it is readily decomposed with liberation of the hydrocarbon when boiled with alkaline solutions, but not by boiling with alcohol.

Pure phenanthrene crystallizes in colourless plates, which have a slight blue fluorescence, and are readily soluble in ether, benzene, carbonic bisulphide, and hot alcohol, crystallizing out from the latter in great part on cooling. It boils at 340° (644° F.), and, according to Ostermayer, melts at 96° (204°·8 F.); Fittig, Ostermayer, and Græbe mention about 100° (212° F.) as the melting point, however.

By heating with hydriodic acid, phenanthrene is converted into phenanthrenetetrahydride (1378). Phenanthrene is less readily oxidized than anthracene, and is converted into *phenanthraquinone*, $C_{14}H_8O_2$, which is isomeric with anthraquinone, but readily distinguished from it by forming compounds with the acid sulphites of the alkali metals. This behaviour renders the detection of phenanthrene very easy. It is simply necessary to dissolve the substance suspected to contain it in glacial acetic acid, and to add a warm solution of chromic anhydride in glacial acetic acid; the oxidation product is first treated with an alkaline solution in order to remove acid substances, and is then warmed with a solution of hydric sodic sulphite. The phenanthraquinone is dissolved, but on the addition of sulphuric or hydrochloric acid, it is precipitated, and may easily be recognised.

Phenanthraquinone is also distinguished from anthraquinone by its conversion into *diphenic acid*, $C_{12}H_8(COOH)_2$, on further oxidation. By the action of nitric acid, phenanthrene is readily converted into nitro-derivatives; it also furnishes *phenanthrenesulphonic acid*, $C_{14}H_9.SO_3H$, when warmed with sulphuric acid, and does not exhibit the tendency to undergo decomposition which is observed when anthracene is similarly treated.

When bromine is added to a well cooled solution of phenanthrene in carbonic bisulphide, very little hydrobromic acid is evolved, and after a time flat prismatic crystals of *phenanthrene dibromide*, $C_{14}H_{10}Br_2$, separate; this decomposes slowly at the ordinary temperature, but rapidly at about 100° (212° F.), with evolution of hydrobromic acid and formation of *monobromophenanthrene*, $C_{14}H_9Br$. The same reaction takes place if the phenanthrene dibromide is boiled with water or with alcohol. Bromophenanthrene crystallizes in slender colourless prisms, which are readily soluble in alcohol, and melt at 63° (145°·4 F.). By the further action of bromine on its solution in carbonic bisulphide it is converted into *dibromophenanthrene*, $C_{14}H_8Br_2$, and *tribromophenanthrene*, $C_{14}H_7Br_3$. They are both colourless substances, the latter crystallizing in silky needles, which melt at 126° (258°·8 F.) (Haydück, *Ann. Chem. Pharm.*, clxvii. 177).

Cold concentrated nitric acid converts phenanthrene into *mononitrophenanthrene*, $C_{14}H_9.NO_2$, which is obtained in the crystalline state by precipitating its acetic acid solution with water. It melts between 70° and 80° (158° and 176° F.). When heated to 100° (212° F.) with strong nitric acid, *dinitrophenanthrene*, $C_{14}H_8(NO_2)_2$, is produced. It separates from its acetic acid solution in yellow crystals, which melt between 150° and 160° (302° and 320° F.) (Græbe).

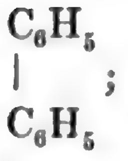
(1392) *Constitution of Phenanthrene.*—When phenanthraquinone is heated with soda-lime, it furnishes almost the theoretical amount of the hydrocarbon *diphenyl* (Græbe), in accordance with the equation:

$$\underset{\text{Phenanthraquinone.}}{C_{14}H_8O_2} + 4NaOH = \underset{\text{Diphenyl.}}{C_{12}H_{10}} + 2Na_2CO_3 + H_2;$$

anthraquinone under similar circumstances yielding benzene:

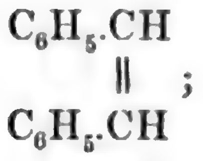
$$C_{14}H_8O_2 + 4NaOH = 2C_6H_6 + 2Na_2CO_3.$$

It is, therefore, inferred that two C_6 groups in phenanthrene are directly united, which is not the case with anthracene, and from this, together with the fact that it may be formed from stilbene, the formula of phenanthrene is written in the following manner:



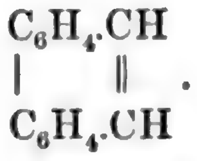
$$\begin{array}{l} C_6H_5 \\ | \\ C_6H_5 \end{array};$$

Diphenyl.



$$\begin{array}{l} C_6H_5.CH \\ \qquad\quad \| \\ C_6H_5.CH \end{array};$$

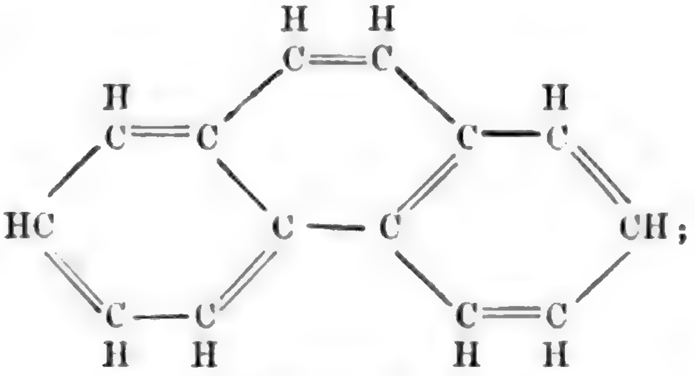
Stilbene.



$$\begin{array}{l} C_6H_4.CH \\ | \qquad\ \ \| \\ C_6H_4.CH \end{array}.$$

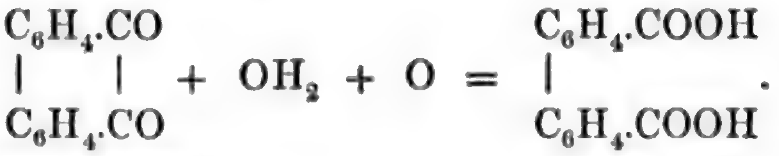
Phenanthrene.

This formula represents phenanthrene as formed from diphenyl by the displacement of two atoms of hydrogen—one in each of the C_6 groups—by the dyad group $HC{=}CH$; but it does not indicate the "position" which this group occupies relatively to the two atoms of carbon, by which the two C_6 groups in diphenyl are linked together. This, however, is shown by the following symbol:



Phenanthrene.

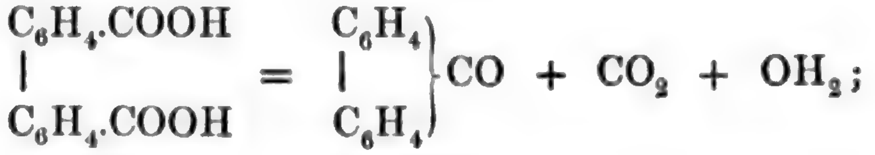
from which it will be seen that the atom of hydrogen eliminated from each of the C_6 groups in the formation of phenanthrene from stilbene is attached to the atom of carbon which is contiguous to the C_2H_2 group; or, in other words, phenanthrene may be regarded as a *diortho*-derivative of diphenyl. The experimental evidence in support of this conclusion is as follows:—It has already been pointed out that on further oxidation phenanthraquinone is converted into diphenic acid:



$$\begin{array}{l} C_6H_4.CO \\ | \qquad\quad | \\ C_6H_4.CO \end{array} + OH_2 + O = \begin{array}{l} C_6H_4.COOH \\ | \\ C_6H_4.COOH \end{array}.$$

Phenanthraquinone. Diphenic acid.

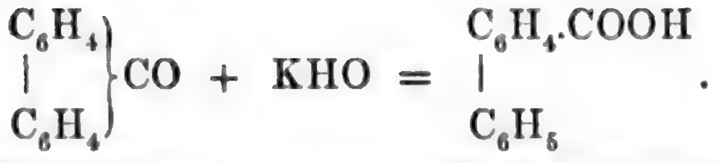
When this acid is distilled with quicklime, it is decomposed in the manner represented by the equation:



$$\begin{array}{l} C_6H_4.COOH \\ | \\ C_6H_4.COOH \end{array} = \left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right\} CO + CO_2 + OH_2;$$

Diphenic acid. Diphenyleneketone.

and by fusing diphenyleneketone with potassic hydrate it is converted into the potassic salt of phenylbenzoic acid:



$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\}CO + KHO = \begin{array}{l}C_6H_4.COOH\\ |\\ C_6H_5\end{array}.$$

Diphenyleneketone. Potassic phenylbenzoate.

The acid so obtained is *not* identical with the *para*phenylbenzoic acid obtained from paracyanodiphenyl (p. 357), and which is also produced on oxidizing paradiphenylbenzene (p. 357); it is therefore probably *ortho*phenylbenzoic acid, since our general experience warrants the conclusion, that it is not likely that phenanthrene is a dimeta-derivative of diphenyl. Admitting it to be *ortho*phenylbenzoic acid, it will be found on tracing out the series of changes by which it is formed with the aid of the graphic symbol above given that there is every reason to regard this symbol as correct.

(1393) TOLANE OR DIPHENYLACETYLENE: $C_6H_5.C{\equiv}C.C_6H_5$ or $C_{14}H_{10}$.—This hydrocarbon was first obtained by Limpricht and Schwanert (*Ann. Chem. Pharm.*, cxl. 330) by heating monobromostilbene, $C_{14}H_{11}Br$, with an alcoholic solution of potassic hydrate, to 130° (266° F.) for ten or twelve hours. It may also be conveniently prepared, according to Fittig (*ibid.* clxviii. 74), from the stilbene dichloride, $C_{14}H_{12}Cl_2$, obtained by the action of phosphorus pentachloride on hydrobenzoïn. When this is boiled with an alcoholic solution of potassic hydrate it is completely converted into tolane.

Tolane forms large transparent prisms, which melt at 60° (140° F.), and distil unchanged at a higher temperature. It is readily soluble in alcohol and ether, and when heated with strong hydriodic acid is reconverted into stilbene and dibenzyl.

Although no brominated or chlorinated derivatives have as yet been obtained from tolane, it readily unites with a molecule of bromine forming *tolane dibromide*, $C_{14}H_{10}Br_2$. This compound exists in two isomeric modifications, one of which crystallizes in small flat needles melting at 200°—205° (392°—401° F.), the other, which is simultaneously produced but in much smaller quantity, in long slender needles, melting at 64° (147°·2 F.). By the action of sodium amalgam on an alcoholic solution of potassic hydrate, they are both reconverted into tolane. If either modification be heated with water for some hours to 170°—180° (338°—356° F.), a considerable quantity of the other modification is produced; and by distilling the isomeride which has the lower melting point, it is in great part converted into that having the higher melting point, and which is scarcely changed on distillation (Limpricht and Schwanert, *Deut. chem. Ges. Ber.*, iv. 379).

When chlorobenzil, $C_{14}H_{10}OCl_2$, is heated with phosphoric pentachloride to 200° (392° F.) the compound $C_{14}H_{10}Cl_4$ (*tolane tetrachloride* or *tetrachlordibenzyl*: $C_6H_5.CCl_2.CCl_2.C_6H_5$) is formed; it is easily converted into tolane by sodium-amalgam, and according to Zinin (*ibid.* iv. 289; *Zeits. Chem.* [2], iv.

718), when treated in alcoholic solution with zinc, it furnishes two isomeric *tolane dichlorides*, $C_{14}H_{10}Cl_2$, one of which crystallizes in rhombic tables melting at 153° (307°·4 F.); the other forms needles which melt at 63° (145°·4 F.). Both these isomerides are likewise produced when stilbene is heated to 170° (338° F.) with phosphorus pentachloride containing a little oxychloride; they yield tolane when treated with sodium-amalgam, or when heated with an alcoholic solution of potassic hydrate to 180° (356° F.), and on distillation are partially converted the one into the other (Limpricht and Schwanert, *loc. cit.*).

The nature of the isomerism which exists between the tolane bromides (or chlorides) has not yet been ascertained; inasmuch, however, as a compound of the formula $C_6H_5.C{\equiv}C.C_6H_5$ can only furnish a single dibromide (or dichloride), viz.: $C_6H_5BrC{=}CBrC_6H_5$, it appears probable that the formation of one of them is the result of isomeric change (see hydrobenzoïn).

(1394) **Methylanthracene**: $C_{15}H_{12}$ or $C_{14}H_9.CH_3 = 192$, is formed when ditolylmethane or dimethyldiphenylmethane (p. 363) is passed over red-hot pumice, two molecules of hydrogen being eliminated. In order to purify it, the product is first washed with ether-alcohol, and then converted into the compound with trinitrophenol. It is also formed on distilling chrysophanic acid and emodin—two substances extracted from rhubarb—with zinc dust (Liebermann, *Deut. chem. Ges. Ber.*, viii. 970, 1102). Methylanthracene crystallizes in white glistening scales which melt at about 200° (392° F.), and sublime unchanged. It is insoluble in water; easily soluble in benzene and carbonic bisulphide, but only slightly soluble in alcohol or ether.

When methylanthracene in carbonic bisulphide solution is treated with bromine, it gives rise to *dibromomethylanthracene*, $C_{15}H_{10}Br_2$, which crystallizes in golden yellow needles melting at 156° (312°·8 F.) (Weiler, *ibid.* vii. 1185; Fischer, *ibid.* vii. 1195). On oxidation with nitric acid, it is converted into *methylanthraquinone*, $C_{14}H_7(CH_3)O_2$, which on further oxidation yields *anthraquinonecarboxylic acid*, $C_{14}H_7O_2(COOH)$.

(1395) **Hydrocarbons**: $C_{16}H_{14} = 206$.—By heating the chloroxylene, $CH_3.C_6H_4.CH_2Cl$, produced by the action of chlorine on boiling coal-tar xylene, with water at 200° (392° F.) and distilling the product, Van Dorp obtained a crystalline hydrocarbon, melting at about 200° (393° F.), which he termed dimethylanthracene (*ibid.* v. 624). It is very improbable, however, that this substance is really a dimethylanthracene, since it is doubtless produced by a series of reactions similar to those which lead to the formation of anthracene from benzylic chloride (p. 372).

Dimethyltolane or Ditolylacetylene: $CH_3.C_6H_4.C{\equiv}CC_6H_4.CH_3. = 206$.—This hydrocarbon is formed when dimethylstilbene dibromide, $C_{16}H_{14}Br_2$, (1385) is heated to 140° (284° F.) with an alcoholic solution of potassic hydrate. It crystallizes in long needles or silvery scales which are rather soluble in alcohol or ether and melt at 136° (276°·8 F.) (Goldschmidt and Hepp, *ibid.* vi. 1505).

(1396) **Retene**: $C_{18}H_{18} = 234$, was discovered by Fikentscher and Trommsdorff in 1837. It is found in fossil coniferous woods, in the higher boiling portions of wood tar, and amongst the products formed on passing the vapour of colophony through a red-hot tube; Berthelot states that it is amongst the substances formed by heating acetylene to redness. It crystallizes in needles or scales which melt at or about 99° (210°·2 F.), and forms with trinitrophenol a compound crystallizing in slender orange coloured needles; on treatment with chromic acid it furnishes several products, the chief of which is *dioxyretistene*, $C_{16}H_{14}O_2$. When dioxyretistene is distilled with zinc dust, *retistene*, $C_{16}H_{14}$, a crystalline hydrocarbon melting at about 94° (201°·2 F.), is obtained (Wahlforss, *Zeits Chem.* [2], v. 73; Ekstrand, *Bull. Soc. Chim.* [2], xxiv. 55).

§ XII. HYDROCARBONS OF THE C_nH_{2n-20} OR BENZYLNAPHTHALENE SERIES.

(1397) Only two hydrocarbons of this series have as yet been obtained, and of these even scarcely anything is known.

Græbe (*Deut. chem. Ges. Ber.*, vii. 782) observed when pure chrysoquinone, $C_{18}H_{10}O_2$, was heated with soda lime that the principal product was a hydrocarbon, $C_{16}H_{12}$, melting at about 105° (221° F.), and readily soluble in alcohol, benzene, and carbonic bisulphide. It is quite possible that this may be *phenylnaphthalene*, $C_{10}H_7.C_6H_5$.

By distilling ruficoccin, a substance obtained by the action of sulphuric acid on the colouring matter of cochineal, with zinc dust, Liebermann and Dorp obtained a crystalline hydrocarbon which probably has the composition $C_{16}H_{12}$ (*Ann. Chem. Pharm.*, clxiii. 112).

Benzylnaphthalene or *naphthylphenylmethane*: $C_{17}H_{14}$ or $C_{10}H_7.CH_2.C_6H_5$ = 218, forms colourless needles which melt at 64° (147°·2 F.), and are insoluble in water but very soluble in ether. It is prepared by the action of zinc powder on a mixture of naphthalene and benzylic chloride (Froté, *Compt. Rend.*, lxxvi. 639).

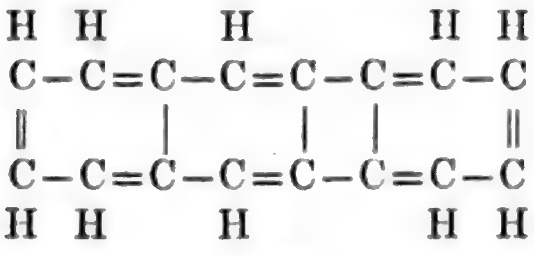
§ XIII. HYDROCARBONS OF THE C_nH_{2n-22} OR PYRENE SERIES.

(1398) Although a number of hydrocarbons of this series have been obtained, comparatively little is known of them. The following is a list:

			M.P. ° Cent.
$C_{16}H_{10}$	Pyrene	$C_{10}H_6(C_6H_4)$	142°
	Diacetenylbenzene . .	$C{\equiv}C.C_6H_5$ | $C{\equiv}C.C_6H_5$	97°
$C_{18}H_{14}$	Paradiphenylbenzene .	$C_6H_4(C_6H_5)_2$	205°
	Orthodiphenylbenzene .		85°
$C_{19}H_{16}$	Triphenylmethane . .	$CH(C_6H_5)_3$	92°
$C_{20}H_{18}$	Paradibenzylbenzene .	$C_6H_4(CH_2.C_6H_5)_2$	86°
	Orthodibenzylbenzene .		78°
	Diphenyltolylmethane .	$CH\begin{cases}(C_6H_5)_2\\C_6H_4.CH_3\end{cases}$	liquid
$C_{21}H_{20}$	Dibenzyltoluenes . .	$CH_3.C_6H_3(CH_2.C_6H_5)_2$	liquid

(1399) PYRENE OR PHENYLENENAPHTHALENE: $C_{16}H_{10}$ or $C_{10}H_6(C_6H_4)$ = 202.—This hydrocarbon appears to have been first observed by Laurent, although he never succeeded in obtaining it in a pure state. Græbe, who subsequently examined it, extracted it from the butyraceous product which comes over after the anthracene in the distillation of coal tar, by treating it with carbonic bisulphide; this dissolves the pyrene and some other hydrocarbons, and leaves the chrysene. The residue left on distilling off the bisulphide is exhausted with warm alcohol, and the cold filtered solution mixed with an alcoholic solution of trinitrophenol or picric acid, which produces a red crystalline precipitate of pyrene picrate, $C_{16}H_{10} + C_6H_3(NO_2)_3OH$. This, after being washed with alcohol, is decomposed by ammonia, and the liberated hydrocarbon crystallized repeatedly from alcohol until it melts at 142° (287°·6 F.). In some instances it is necessary to reconvert it into the picrate and again decompose it. The picrate crystallizes in long red needles, which are only slightly soluble in cold alcohol, but readily in ether and carbonic bisulphide, and very easily in benzene.

Pure pyrene usually forms colourless scales, but by slow evaporations of its solutions it may be obtained in large rhombic plates. It sublimes with difficulty, and distils at a temperature considerably above 360° (680° F.). By heating with hydriodic acid solution and phosphorus at 200° (392° F.), it is converted into pyrenehexahydride (p. 369). Pyrene is oxidized with considerable difficulty, and converted into *pyrenequinone*, $C_{16}H_8O_2$, which has properties similar to those of anthraquinone. Pyrene, in fact, exhibits very considerable resemblance to anthracene, and it therefore appears probable that it has a similar "constitution;" the following symbol may provisionally be employed to represent it:



Pyrene.

Dibromopyrene dibromide, $C_{16}H_8Br_4$, is formed when the finely-divided hydrocarbon is exposed to the action of bromine vapour at the ordinary temperature. It crystallizes from nitrobenzene in pale yellow needles, which are almost insoluble in alcohol, ether, or benzene. *Tribromopyrene*, $C_{16}H_7Br_3$, is precipitated on adding bromine in slight excess to a solution of pyrene in carbonic bisulphide. It forms colourless needles which closely resemble the compound just described.

When pyrene is heated with nitric acid (s.g. 1·2), diluted with an equal volume of water, it is converted into a reddish oil which solidifies on cooling. This, when crystallized from alcohol, yields yellow needles of *mononitropyrene*, $C_{16}H_9.NO_2$. They are easily soluble in ether or benzene and melt at about 140°

(284° F.). *Dinitropyrene*, $C_{16}H_8(NO_2)_2$, forms slender yellow needles which are only slightly soluble in alcohol, ether, and benzene. It is prepared by boiling pyrene with nitric acid of specific gravity 1·45, exhausting the product with boiling alcohol to remove any of the mononitro-derivative, and finally crystallizing from acetic acid. *Tetranitropyrene*, $C_{16}H_6(NO_2)_4$, is formed when dinitropyrene is digested for a long time with fuming nitric acid. It crystallizes from acetic acid in long needles (Græbe, *Ann. Chem. Pharm.*, clviii. 285).

(1400) DIACETENYLBENZENE or DIPHENYLDIACETYLENE: $C_{16}H_{10}$ or $C_6H_5.C\equiv C.C\equiv C.C_6H_5 = 202$.—This hydrocarbon, discovered by Glaser (*Deut. chem. Ges. Ber.*, ii. 423), is formed when the copper derivative of acetenylbenzene, $C_6H_5.C\equiv C.Cu_2.C\equiv C.C_6H_5$, is suspended in an alcoholic solution of ammonia and agitated in contact with air. On diluting the alcoholic solution with water, the new compound separates in glistening needles. It melts at 97° (206°·6 F.), and is easily soluble in alcohol or ether, but not in water. No derivatives have as yet been obtained from it; but when exposed to an atmosphere charged with bromine, it takes up four molecules of the latter forming a viscous compound.

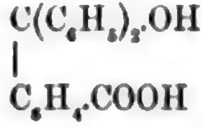
(1401) PARADIPHENYLBENZENE: $C_{18}H_{14}$ or $C_6H_4(C_6H_5)_2 = 230$.—Riese (*Ann. Chem. Pharm.*, cxliv. 161) obtained this substance, mixed with diphenyl and an amorphous brominated derivative, by the action of sodium on the solid paradibromobenzene dissolved in anhydrous ether; whilst Schultz (*ibid.* clxxiv. 230) observed it amongst the products formed when benzene is passed through red-hot tubes. It crystallizes from benzene, in which it is easily soluble, in flat colourless needles, melting at 205° (401° F.). It does not combine with trinitrophenol, and is only very slightly soluble in boiling alcohol. On oxidation, it is first converted into *paraphenylbenzoic acid*, $C_6H_5.C_6H_4.COOH$, and ultimately into terephthalic acid, $C_6H_4(COOH)_2$.

Schultz also obtained a small quantity of an isomeric hydrocarbon which he terms *isodiphenylbenzene*, melting at 85° (185° F.); it furnishes benzoic acid on oxidation, and is very probably *ortho*diphenylbenzene.

(1402) TRIPHENYLMETHANE: $C_{19}H_{16}$ or $CH(C_6H_5)_3 = 244$.—Kekulé and Franchimont (*Deut. chem. Ges. Ber.*, v. 906) first obtained this hydrocarbon by heating one molecule of (0–2) dichlorotoluene, $C_6H_5.CHCl_2$, with two of mercury phenyl, $Hg(C_6H_5)_2$, and it has since been prepared by Hemilian (*ibid.* vii. 1203) by heating a mixture of benzene and diphenylcarbinol or benzhydrol, $CH(C_6H_5)_2.OH$, with phosphoric anhydride at 140° (284° F.) for four hours. It is easily purified by crystallizing it from boiling alcohol, when it forms thin lustrous plates, melting at 92° (197°·6 F.), and distilling undecomposed at 360° (680° F.). By the action of nitric acid it is converted into the trinitro-derivative $CH(C_6H_4.NO_2)_3$. On adding bromine to its solution in carbonic bisulphide, the bromo-derivative, $CBr(C_6H_5)_3$, is produced, and remains as an oil on distilling off the bisulphide; on treating this oil with water, it solidifies to a crystalline mass of *triphenylcarbinol*, $C(C_6H_5)_3.OH$, which is also produced when the hydrocarbon is boiled with an oxidizing mixture of potassic dichromate and sulphuric acid. The corresponding *triphenylchloromethane*, $CCl(C_6H_5)_3$, is formed by the action of phosphoric pentachloride on triphenylcarbinol; it is crystalline, and is readily reconverted into triphenylcarbinol by warming with water.

(1403) HYDROCARBONS: $C_{20}H_{18} = 258$.—By the action of benzylic chloride on benzene in presence of zinc, two isomeric *dibenzylbenzenes*, $C_6H_4(CH_2.C_6H_5)_2$, are produced, together with benzylbenzene. *Paradibenzylbenzene* crystallizes from hot alcohol, in which it is easily soluble, although cold alcohol dissolves it with difficulty, in thin, flat, glistening plates, which melt at 86° (186°·8 F.); on oxidation it yields *paradibenzoylbenzene*, $C_6H_4(CO.C_6H_5)_2$, together with a small quantity of *parabenzoylbenzoic acid*. *β*- or *orthodibenzylbenzene* is far more soluble than the isomeride, and crystallizes in long, thin, flat needles, which melt at 78° (172°·4 F.); when oxidized it furnishes β- or *orthodibenzoylbenzene* and β- or *orthobenzoylbenzoic acid*. These hydrocarbons do not combine with trinitrophenol. Paradibenzylbenzene is also obtained together with traces of the isomeride in the preparation of benzylbenzene, by Baeyer's method, from benzene and methylal (p. 360) (Zincke, *ibid.* vi. 119; ix. 31).

By heating a mixture of diphenylcarbinol and toluene with phosphoric anhydride, Hemilian obtained a *diphenyltolylmethane*, $CH_3.C_6H_4.CH(C_6H_5)_2$, as a liquid of high boiling point which does not solidify even in a freezing mixture; on oxidation it is converted into the acid



$$\begin{array}{l} C(C_6H_5)_2.OH \\ | \\ C_6H_4.COOH \end{array}$$

(*ibid.* vii. 1209).

(1404) HYDROCARBONS: $C_{21}H_{20} = 272$.—The portion boiling at 292°—296° (557°—565° F.) separated by careful fractional distillation from the product of the action of benzylic chloride on toluene in presence of zinc (p. 362), is a mixture of two, or perhaps of three isomeric $C_{21}H_{20}$ hydrocarbons, since it yields two isomeric acids of the composition $C_{21}H_{14}O_4$, and a third of the composition $C_{15}H_{10}O_6$, on oxidation. The two C_{21} acids are isomeric *dibenzoylbenzoic acids*, $C_6H_3(CO.C_6H_5)_2.COOH$; the nature of the third acid has not been ascertained, and it may either be derived from a special $C_{21}H_{20}$ hydrocarbon, or perhaps it is formed by the further oxidation of one of the dibenzoylbenzoic acids (Zincke and Weber, *ibid.* vii. 1153). When the mixture of $C_{21}H_{20}$ hydrocarbons is passed through a red-hot tube, hydrogen, toluene, and anthracene are produced, and also an isomeride of anthracene, of which as yet only small quantities have been obtained.

§ XIV. HYDROCARBONS OF THE C_nH_{2n-24} OR CHRYSENE SERIES.

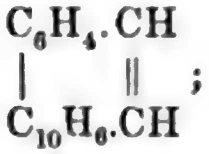
(1405) Only two members of this series are at present known, namely, *chrysene*, $C_{18}H_{12}$, and *phenylenediphenylmethane*, $C_{19}H_{14}$.

CHRYSENE: $C_{18}H_{12} = 228$.—This hydrocarbon was first observed by Laurent in crude anthracene, and Berthelot has stated that it is produced when benzene is passed through a red-hot tube. This, perhaps, is somewhat doubtful, as from the subsequent experiments of Schultz (*Ann. Chem. Pharm.*, clxxiv. 230) and of Schmidt (*Deut. chem. Ges. Ber.*, vii. 1365), it would seem that Berthelot's chrysene was really impure diphenylbenzene; nevertheless, in a recent paper (*Bull. Soc. Chim.* [2], xxii. 437), Berthelot reasserts that under these circumstances he obtains a hydrocarbon of the formula $C_{18}H_{12}$, which forms a compound with trinitrophenol.

In order to prepare chrysene from the semi-solid higher boiling portions of coal-tar, it is first treated with carbonic bisulphide to remove pyrene and other soluble hydrocarbons, and the solid residue is then crystallized from coal-oil boiling at 150° (302° F.). It is, however, still of a bright yellow colour, but may be obtained colourless by boiling it with alcohol and a small quantity of nitric acid, or by heating it to 240° (464° F.)

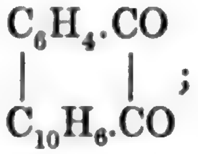
with hydriodic acid and amorphous phosphorus. Pure colourless chrysene may also be obtained by reducing the compound of dinitroanthraquinone and chrysene, formed by the action of nitric acid on an alcoholic solution of anthracene and chrysene, with tin and hydrochloric acid (Schmidt, *Journ. pr. Chem.* [2], ix. 270). Chrysene crystallizes from benzene or acetic acid in plates belonging to the rhombic system, and which melt at about 250° (482° F.). It cannot be sublimed without decomposition. It combines with trinitrophenol or picric acid, forming a compound $C_{18}H_{12} + C_6H_2(NO_2)_3.OH$, which crystallizes in orange-coloured needles, and is easily decomposed by cold alcohol (Liebermann, *Ann. Chem. Pharm.*, clviii. 299; Schmidt, *loc. cit.*).

Chrysene is oxidized with very great readiness by chromic acid and converted into *chrysoquinone*, $C_{18}H_{10}O_2$: if the action of the oxidizing agent be continued phthalic acid is also produced. Chrysoquinone closely resembles phenanthraquinone in its properties, and it is not improbable therefore that the constitution of chrysene is very similar to that of phenanthrene, and that it may be represented by the formula:



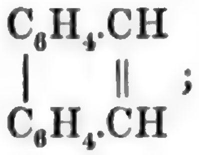
$\begin{array}{l} C_6H_4.CH \\ | \qquad \| \\ C_{10}H_6.CH \end{array}$;

Chrysene.



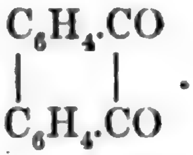
$\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_{10}H_6.CO \end{array}$;

Chrysoquinone.



$\begin{array}{l} C_6H_4.CH \\ | \qquad \| \\ C_6H_4.CH \end{array}$;

Phenanthrene.



$\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_6H_4.CO \end{array}$.

Phenanthraquinone.

Dichlorochrysene, $C_{18}H_{10}Cl_2$, which crystallizes from benzene in colourless needles, is formed on treating chrysene with chlorine at 100°. It melts at 267° (512°6 F.) and is almost insoluble in alcohol or ether. Higher chlorinated derivatives are produced by the action of chlorine at 160°—170° (320°—338° F.), but they have not been examined. On adding bromine to chrysene dissolved in carbonic bisulphide, no action is at first perceptible, but after a time hydrobromic acid is evolved and white needles of *dibromochrysene*, $C_{18}H_{10}Br_2$, separate; it melts at 273°, and on oxidation is converted into chrysoquinone. When chrysene is exposed to an atmosphere of bromine vapour, higher brominated derivatives are formed, but these have not been isolated in a pure state; there appears, however, to be no tendency on the part of chrysene to form additive compounds.

Mononitrochrysene, $C_{18}H_{11}.NO_2$, is formed when chrysene is boiled with alcohol and nitric acid, or more rapidly by heating it with nitric acid (sp. gr. 1·25) at 100° (212° F.); it crystallizes from benzene in thick yellow prisms which melt at 209° (408°·2 F.). When finely divided chrysene is boiled with nitric acid (sp. gr. 1·3), it is converted into a mixture of the mono-, di- and tetranitro-derivatives. *Dinitrochrysene*, $C_{18}H_{10}(NO_2)_2$, crystallizes from acetic acid in yellow needles which melt above 300° (572° F.) and are almost insoluble in alcohol, ether, and benzene. The *tetranitrochrysene*, $C_{18}H_8(NO_2)_4$, which likewise forms yellow needles, is also produced by boiling the hydrocarbon with fuming nitric acid (Liebermann, Schmidt).

(1406) *Phenylenediphenylmethane*: $C_{19}H_{14}$ or $C(C_6H_5)_2(C_6H_4) = 245$.— When the triphenylchloromethane, $CCl(C_6H_5)_3$, obtained by the action of phosphoric pentachloride on triphenylcarbinol (1402) is heated to about 200° (392° F.), it is decomposed with evolution of hydrochloric acid, and at a higher temperature an oil distils over, which on cooling solidifies to a crystalline mass. It is but slightly soluble in alcohol or acetic acid, crystallizing from the latter in slender silky needles which melt at 138° (280°·4 F.). It has the composition represented by the formula $C_{19}H_{14}$, and from the mode of its formation there can be no doubt it is a phenylenediphenylmethane (Hemilian, *Deut. chem. Ges. Ber.*, vii. 1208).

§ XV. HYDROCARBONS OF THE C_nH_{2n-26} OR DINAPHTHYL SERIES.

Three members of this series are known, viz.:

			M.P. ° Cent.
$C_{20}H_{14}$	Dinaphthyl Isodinaphthyl	$(C_{10}H_7)_2$	154° 187°
$C_{21}H_{16}$	Dinaphthylmethane	$CH_2(C_{10}H_7)_2$	109°

(1407) **DINAPHTHYL:** $C_{20}H_{14}$ or $C_{10}H_7.C_{10}H_7 = 254$. — This hydrocarbon, which was discovered by Lossen (*Ann. Chem. Pharm.*, cxliv. 71), forms pale yellow scales when crystallized from alcohol, whilst from a mixture of ether and alcohol it is deposited in octohedra: it melts at 154° (309°·2 F.), and boils above 360° (680° F.) It is formed, along with phthalic acid and resinous products, when naphthalene is heated with manganic dioxide and sulphuric acid diluted with twice its weight of water, and also, although in exceedingly small quantity, by the action of sodium on a solution of bromonaphthalene in benzene. The latter mode of formation renders it probable that dinaphthyl is an *a*-derivative of naphthalene.

By the action of bromine it is first converted into *dibromodinaphthyl*, $C_{20}H_{12}Br_2$, which crystallizes in delicate monoclinic prisms melting at 215° (419° F.). It is almost insoluble in alcohol, but easily soluble in hot benzene. An amorphous yellow *hexabromodinaphthyl*, $C_{20}H_8Br_6$, is obtained when excess of bromine is used. A yellow resinous *hexachlorodinaphthyl*, $C_{20}H_8Cl_6$, is formed on passing chlorine to saturation into a solution of dinaphthyl in carbonic bisulphide. A resinous *tetranitrodinaphthyl*, $C_{20}H_{10}(NO_2)_4$, is precipitated on adding water to a solution of the hydrocarbon in fuming nitric acid.

(1408) **ISODINAPHTHYL:** $C_{20}H_{14} = 254$.—W. Smith (*Journ. Chem. Soc.*, xxiv. 1184) found that a hydrocarbon of high boiling point was formed in minute quantity when naphthalene is passed through an iron tube heated to bright redness; he has since ascertained that it is far more readily produced when a mixture of the vapours of naphthalene and antimonious chloride is passed through a red-hot tube. It is readily separated from accompanying naphthalene by fractional distillation, as it boils above

360° (680° F.). When carefully sublimed it may be obtained in delicate plates, which melt at 187° (368°·6 F.). With chlorine it yields a colourless amorphous *tetrachlorisodinaphthyl*, $C_{20}H_{10}Cl_4$. Bromine attacks it violently, forming *heptabromisodinaphthyl*, $C_{20}H_7Br_7$.

(1409) Dinaphthylmethane: $C_{21}H_{16}$ or $CH_2(C_{10}H_7)_2 = 268$.—In order to prepare this hydrocarbon, 5 parts of naphthalene are dissolved in 20 of chloroform and mixed with 1 of methylal: 10 parts of sulphuric acid are then gradually and cautiously added, preventing rise of temperature by keeping the flask in cold water. After twelve hours, 30 parts of water are added, the chloroform distilled off, and the product purified by exhausting it with boiling ether and distilling the residue. It crystallizes from boiling alcohol in short colourless prisms which melt at 109° (228°·2 F.) and boil at above 360° (680° F.) It is very soluble in ether, benzene, and chloroform, and dissolves in 15 parts boiling and 120 of cold alcohol. With trinitrophenol it forms a compound which crystallizes in reddish-yellow prisms melting at about 142° (287°·6 F.).

On adding bromine to an ethereal solution of the hydrocarbon, hydrobromic acid is given off, and an oily liquid is obtained which soon solidifies to a crystalline mass of *dibromodinaphthylmethane*, $C_{21}H_{14}Br_2$. It forms short colourless needles melting at 193° (379°·4 F.), and which are moderately soluble in ether, benzene, and chloroform, but with difficulty in alcohol.

Tetranitrodinaphthylmethane, $C_{21}H_{12}(NO_2)_4$, forms small rhombic crystals which are almost colourless. It is readily prepared by dissolving the hydrocarbon in 10 parts of fuming nitric acid and allowing it to stand for 12 hours, when the nitro-compound separates in the crystalline state. It is almost insoluble in alcohol, ether, and benzene, but may be dissolved in aniline (T. Grabowski, *Deut. chem. Ges. Ber.*, vii. 1605).

Dinaphthyltrichlorethane, $CCl_3.CH(C_{10}H_7)_2$, which may be regarded as a derivative of the unknown hydrocarbon *β-dinaphthylethane*, $CH_3.CH(C_{10}H_7)_2$, is obtained on treating a mixture of chloral and naphthalene with concentrated sulphuric acid. It crystallizes in colourless hexagonal plates which are moderately soluble in ether, but only slightly so in alcohol (Grabowski, *ibid.* vii. 225).

§ XVI. Hydrocarbons of the C_nH_{2n-28} Series.

(1410) The only member of this series which has, as yet, been prepared is *a-dinaphthylethylene*: $C_{22}H_{16}$ or $C_{10}H_7.HC{=}CH.C_{10}H_7 = 280$, and even that has been but very imperfectly examined. When the crude *dinaphthylmonochlorethane* obtained by the action of sulphuric acid on a mixture of dichlorether and naphthalene is distilled, an oil is obtained boiling above 360° (680° F.), and which, on oxidation, appears to give naphthoic acid (Hepp, *Deut. chem. Ges. Ber.*, vii. 1419).

On boiling dinaphthyltrichlorethane (1409) with an alcoholic solution of potassic hydrate, a yellow substance is obtained, which has the composition of a *dichlorodinaphthylethylene*. It is either a derivative of the hydrocarbon just described, or more probably of an isomeric hydrocarbon, *β-dinaphthylethylene*, $H_2C{=}C(C_{10}H_7)_2$ (Grabowski, *ibid.* vii. 225).

§ XVII. Hydrocarbons of the C_nH_{2n-30} or Idrialene Series.

Four members of this series are at present known, viz.:

			M.P. ° Cent.
$C_{22}H_{14}$	Idrialene	——	285°
$C_{24}H_{18}$	Triphenylbenzene	$C_6H_3(C_6H_5)_3$	170°
$C_{25}H_{20}$	Tetraphenylmethane	$C(C_6H_5)_4$	145°
$C_{26}H_{22}$	Tetraphenylethane	$C_2H_2(C_6H_5)_4$	206°

(1411) **Idrialene**: $C_{22}H_{14} = 278$.—This hydrocarbon, about which very little is known, exists in the mineral *idrialite*, a substance resembling coal, which is found in the Idrian mercury mines. It may be extracted by distillation in an atmosphere of carbonic anhydride, or preferably by exhausting the mineral with benzene, and concentrating the solution by distillation. It crystallizes in colourless scales, which melt above 285° (545° F.), and volatilize at a higher temperature, but with decomposition. Nitric acid converts it into *trinitro-idrialene*, $C_{22}H_{11}(NO_2)_3$, and on oxidation with chromic acid, it yields *idria-quinone*, $C_{22}H_{12}O_2$. Idrialene is the fifth term in the series, including benzene, naphthalene, anthracene and phenanthrene, and chrysene, which differ by nC_4H_2, and all of which furnish quinones.

(1412) **Triphenylbenzene**: $C_{24}H_{18}$ or $C_6H_3(C_6H_5)_3 = 306$.—This hydrocarbon was first discovered by Engler and Heine (*Deut. chem. Ges. Ber.*, vi. 641) amongst the products of the action of ammonia and phosphoric anhydride on methylphenylketone or acetophenone:

$$\underset{\text{Methylphenylketone.}}{3C_6H_5.CO.CH_3} = \underset{\text{Triphenylbenzene.}}{C_6H_3(C_6H_5)_3} + 3OH_2,$$

and has since been prepared by the action of dry hydrochloric acid on the same ketone (Engler and Berthold, *ibid.* vii. 1123; Heyne, viii. 230; and Engler, viii. 394). The gas is rapidly absorbed with evolution of heat, and, on allowing the solution to stand for a day or two in a warm place, the hydrocarbon is deposited in the crystalline state. The formation of triphenylbenzene in this manner is comparable with that of mesitylene from dimethylketone (p. 265). It forms large colourless rhombic plates, which melt at about 170° (338° F.), and boil at a much higher temperature. It is only moderately soluble in alcohol, ether, and carbonic bisulphide, somewhat more readily in benzene.

Monobromotriphenylbenzene, $C_{24}H_{17}Br$, produced by the action of bromine on the hydrocarbon in carbonic bisulphide solution, forms colourless needles, which melt at 104° (219°·2 F.). A *trinitrotriphenylbenzene*, $C_{24}H_{15}(NO_2)_3$, has been obtained in crystalline scales, but its preparation is attended with considerable difficulties (Engler and Berthold).

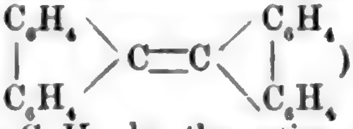
(1413) **Tetraphenylmethane**: $C_{25}H_{20}$ or $C(C_6H_5)_4 = 320$.—This hydrocarbon is found, according to Behr (*ibid.* v. 971), amongst the products of the dry distillation of baric benzoate, and it would also seem to be produced, although in much smaller quantity, when the calcic salt is distilled (Kekulé and Franchimont, *ibid.* vi. 910). It crystallizes from alcohol in long colourless needles, which melt at about 145° (293° F.).

(1414) **α-Tetraphenylethane**: $C_{26}H_{22}$ or $CH(C_6H_5)_2.CH(C_6H_5)_2 = 334$.—On heating benzopinacone, $C(OH)(C_6H_5)_2.C(OH)(C_6H_5)_2$, with hydriodic acid and phosphorus at a high temperature for 6 or 8 hours, it is reduced with formation of the hydrocarbon $C_{26}H_{22}$, which may readily be separated from the unaltered pinacone by treatment with alcohol It is only slightly soluble in boiling alcohol, but easily in hot benzene. It crystallizes in large prisms, which melt at 206° (402°·8 F.), and, at a higher temperature, sublime readily in needles and small plates. Substitution derivatives are produced by the action of bromine and of nitric acid, but, as yet, they have not been examined (Græbe, *ibid.* viii. 1055). It is also formed by the action of heat on diphenylchloromethane (1377).

§ XVIII. Hydrocarbons of the C_nH_{2n-32} or Tetraphenylethylene Series.

(1415) Tetraphenylethylene: $C_{26}H_{20}$ or $(C_6H_5)_2C{=}C(C_6H_5)_2 = 332$.—This hydrocarbon is the only known member of the series. To prepare it, diphenyldichloromethane, $CCl_2(C_6H_5)_2$, is mixed with finely divided silver, obtained by reducing argentic chloride with zinc: a powerful action takes place, with development of heat, which must be moderated at first by cooling in order to avoid decomposition of the chloride. The product is distilled as soon as the reaction is finished, when benzophenone passes over first, and afterwards the hydrocarbon, which solidifies on cooling to a crystalline mass. It is very difficultly soluble in alcohol or ether, but readily in hot benzene, from which it separates on cooling in spicular prisms, melting at 221° (429°·8 F.) (Behr, *ibid.* iii. 752). The same hydrocarbon is found amongst the products obtained when benzophenone is heated with zinc dust (Staedel, *ibid.* vi. 1401).

§§ XIX and XX. Hydrocarbons of the C_nH_{2n-34} and C_nH_{2n-36} Series.

When fluorene is distilled over heated plumbic oxide, a hydrocarbon of the composition $C_{26}H_{16}$ (?  $\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}\!\!>C{=}C<\!\!\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}$) is obtained, which is converted into the hydrocarbon $C_{26}H_{18}$ by the action of sodium-amalgam on its boiling alcoholic solution (Harpe and Dorp, *ibid.* viii. 1048). Neither has been examined, however, and their formation is chiefly of interest on account of their containing relatively more carbon than any other of the known hydrocarbons.

General Review of the Hydrocarbons.

(1416) It is of especial importance and interest to compare the various series of isologous hydrocarbons, so as to ascertain in what respects they resemble each other, and also to observe the points in which they differ; for by so doing we obtain an insight into the laws which regulate the formation of compounds of carbon and hydrogen, and we are also enabled to form some idea of the relation which undoubtedly obtains between composition and chemical properties. At the same time, many questions in connexion with this subject which could not be dealt with advantageously at an earlier stage, may now be considered.

We notice in the first place, that if we merely regard the empirical composition of the isologous hydrocarbons, each particular series appears to bear the same relation to the preceding or next following, but this is by no means the case when their properties are contrasted. Not only is this so with the isologous hydrocarbons, but it is also the case with the homologous hydrocarbons owing to the occurrence of isomerism. We may, in fact, regard bodies as homologous and isologous in a *broad sense,* understanding merely thereby that they exhibit a constant difference in empirical composition; and as *strictly* homologous and isologous when they not only exhibit corresponding differences in composition, but have also certain chemical properties in common. Thus the hydrocarbons of the olefine and acetylene series are true isologues of the paraffins: they are formed from the latter by the withdrawal of two and four atoms of hydrogen respectively, and are readily reconverted into paraffins or paraffin derivatives; combining, for example, with the number of atoms of bromine requisite to convert them into bromo-paraffins. In fact, the differences which result from the withdrawal of two atoms of hydrogen from the paraffins in the formation of the olefines, may be said to be extended in the same direction by the withdrawal of a second pair in the formation of the acetylenes from the olefines. The same is true of valylene, the lowest term of the C_nH_{2n-4} series, which combines with six atoms of bromine, and of dipropargyl, the isomeride of benzene, which combines with eight atoms of bromine; so that these hydrocarbons also are terms of series which are truly isologous with the acetylene, olefine and paraffin series. But if we compare the $C_{10}H_{16}$ hydrocarbons or terpenes with valylene, it is evident that they are not strictly speaking homologous, but rather belong to a parallel homologous series; they exhibit, however, the very closest resemblance to benzene and its homologues, which also cannot strictly be considered as members of the same homologous series as dipropargyl, and may therefore be regarded as members of a series strictly isologous with that which includes benzene. In explanation of this, it is supposed that in the paraffins, olefines, acetylenes, valylene and dipropargyl, the carbon atoms are so united that they form an "open chain," whereas in the terpenes, and benzene and its homologues, the carbon atoms form a "closed chain;" this convenient hypothesis being founded chiefly on the behaviour of the hydrocarbons of the various series with chlorine or bromine. In the paraffins, no carbon atom is united to another by more than one of its four affinities, and the action of chlorine or bromine on these hydrocarbons invariably produces *substitution* derivatives containing the same number of carbon atoms; whereas the olefines, acetylenes, valylene and dipropargyl *combine* with these halogens: but at most with 2, 4, 6 or 8 atoms respectively, being ultimately converted into the haloid paraffin derivatives containing the same number of carbon atoms. We are thus led to the important conclusion that, in general, when hydrocarbons are submitted to the action of chlorine or bromine, these halogens are unable to split apart carbon atoms united by single affinities; and that when the carbon atoms are held together by two or three affinities, they may readily be *partially*, but never *entirely* disunited.*

When six atoms of carbon are arranged in the simplest possible manner so as to form a closed chain or ring, each atom will be united to the next by one of its affinities. Since in this manner two of the affinities of each carbon atom will be engaged, the complex will be capable of combining with at most twelve monad atoms; this is the case with benzene, which can only combine with six atoms of chlorine or bromine, whereas dipropargyl, its isomeride, in which the chain is open,* can unite with eight atoms. It is especially noteworthy that the closing up of the chain, not only lowers the absolute combining power of the complex by two units, but reduces its energy or tendency to combine, in a far greater proportion. Thus the hydrocarbons of the olefine and acetylene series, as well as valylene and dipropargyl, very readily combine with bromine, much heat being developed when the substances are brought into contact; whereas benzene unites with bromine to form the hexabromide only under exceptional conditions, the aid of light being necessary to effect the combination.

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* Under certain special conditions, however, when a large proportion of the negative element is accumulated in the compound, *i.e.*, when the whole, or at least the greater part of the hydrogen is displaced by chlorine, the severance of the carbon atoms which are united by single affinities does take place. Thus by heating *a*-chloropropane, C_3H_7Cl, with iodine chloride, finally at a temperature of 200° (392° F.), it is converted into octochloropropane, C_3Cl_8, which by the further action of the iodine chloride at 250° (482° F.), is resolved into hexachlor-

Many of the hydrocarbons of the remaining series are allied to the paraffins, olefines, or acetylenes; although most of them exhibit properties which indicate that they are also closely related to benzene or its homologues. Thus cinnamene and its homologues, and acetenylbenzene, bear a precisely similar relation to the corresponding terms of the benzene series, that the olefines and acetylenes bear to the corresponding paraffins; and the relation between tolane, the hydrocarbons of the stilbene series, and the corresponding terms of the diphenyl series, is of a precisely similar character to that which obtains between the hydrocarbons of the acetylene, olefine and paraffin series; but by their behaviour on oxidation, and in many cases towards concentrated nitric and sulphuric acid, these hydrocarbons betray their connexion with benzene and its homologues. The assumption that the hydrocarbons in question are formed from the paraffins, olefines or acetylenes, by the introduction in place of hydrogen of monad radicles derived from benzene or its homologues, at once furnishes an explanation of their behaviour.

This is also the case with certain benzene derivatives such as (o—1) chlorotoluene or benzylic chloride, $C_6H_5.CH_2Cl$, which in many of its reactions is strictly analogous to the α-chloroparaffins; $CH_3.CH_2Cl$, or chlorethane, for example. In fact, wherever a paraffin residue enters into the composition of a hydrocarbon, that hydrocarbon will have some properties in common with the paraffins, olefines, &c., and may occasionally for the sake of convenience be regarded as a paraffin or olefine derivative.

Certain hydrocarbons such as naphthalene, diphenyl, anthracene and phenanthrene, pyrene, chrysene, and dinaphthyl, exhibit properties which indicate that they are in no simple way related to the paraffins, but that, on the con-

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ethane, C_2Cl_6, and tetrachloromethane, CCl_4; similarly, β-chlorotetrane (isoprimary butylic chloride), C_4H_9Cl, is converted by heating with iodine chloride, finally at 240 (464° F.), into octochloropropane and tetrachloromethane (Krafft and Merz, *Deut. chem. Ges. Ber.*, viii. 1296). It is especially noteworthy that hexachlorobenzene, in which it is supposed the carbon atoms are united by one and two affinities of each alternately, is not in the least affected by heating with iodine chloride even at 300° (572° F.).

* The student should remember that all language of this kind is not to be interpreted absolutely, being rather the expression of our ignorance than of our knowledge. The hypothesis of which such language is exponent is merely employed to enable us to give a consistent explanation of the relations of the various classes of bodies to one another, and to indicate the points in which they differ from, or resemble one another.

trary, they are allied more or less closely to benzene. It is therefore probable that their constitution is similar to that of benzene; and just as the carbon atoms in benzene are supposed to be united so as to form a closed chain, having as it were but a single loop, the carbon atoms in these hydrocarbons are also assumed to be united so as to form a closed chain, the chain consisting, however, of two or more loops, as in the case of naphthalene (p. 348), anthracene (p. 374), phenanthrene (p. 380), pyrene (p. 384), &c.

It is very remarkable that although these hydrocarbons contain relatively much less hydrogen than benzene, they nevertheless combine with far fewer atoms of bromine or chlorine. Thus naphthalene unites with at most four atoms of chlorine, and anthracene furnishes dibromanthracene tetrabromide when exposed to the action of an excess of bromine, although theoretically, if these hydrocarbons were capable of being raised to the type of the paraffins, we might expect them to unite with 10 and 14 monad atoms respectively. Phenanthrene only combines with two atoms of bromine, and pyrene is converted into dibromopyrene dibromide by an excess of bromine; lastly, chrysene does not appear to furnish additive compounds with bromine. Benzene, naphthalene, anthracene with its isomeride phenanthrene, and chrysene, may be regarded as forming a series the terms of which differ from each other by $n\text{C}_4\text{H}_2$. Although their quinones, except that of anthracene, closely resemble one another, yet it will be seen that the hydrocarbons themselves differ, but progressively in the same direction. Benzene, for example, is capable of combining with six atoms of bromine; naphthalene unites with four; and phenanthrene with two; whilst chrysene appears to be incapable of uniting with bromine. From this it would seem that the formation of each new loop in the chain of carbon atoms tends to reduce the combining power by two units, since naphthalene and anthracene, each of which has two loops, combine with two atoms of bromine less than benzene, which has only a single loop, and phenanthrene and pyrene, which have three loops, combine with four atoms less than benzene.* The additive compounds of the halogens with naphthalene, anthracene, phenanthrene, pyrene and chrysene are far more readily produced than the benzene compounds, and do not require the intervention of light. As experiments have not yet been made to ascertain what would be the behaviour of these hydrocarbons under conditions similar to those which lead to the production of benzene hexabromide and hexachloride, it would be premature to attempt to draw conclusions from this difference; but the subject is well worthy of attention and investigation.

It is a question whether the haloid substitution derivatives of hydrocarbons of the series isologous with the paraffins are in any case *directly* produced, as we suppose the substitution derivatives of the paraffins to be, or whether their formation is not always preceded by that of additive compounds. It is beyond doubt that additive compounds are first formed in the case of the hydrocarbons of the series intermediate between the paraffins and the benzenes, and also from hydrocarbons such as naphthalene and anthracene. The behaviour of benzene itself justifies a similar conclusion, although the extraordinary facility with which chloro- and bromo-substitution derivatives of its higher homologues are formed, especially from mesitylene, tends rather to favour the impression that they are produced without the intervention of additive compounds. The ready formation of dibromodiphenyl by the mere addition of bromine to the hydrocarbon suspended in water is also remarkable in this respect. It must be borne in mind, however, that the lower bromine additive compounds are extremely unstable bodies, and that their formation is therefore very likely to escape notice. Thus although benzene hexabromide, $C_6H_6Br_6$, is a very stable substance, the lower compounds, $C_6H_6Br_2$ and $C_6H_6Br_4$ (which have never been isolated), are apparently very unstable, the application of a very slight degree of heat sufficing to decompose them.* Similarly, although additive compounds of naphthalene and anthracene with chlorine are known, corresponding bromine compounds have not been obtained, naphthalene yielding mono- and dibromonaphthalenes, and anthracene being converted, even by minimum quantities of bromine, into dibromanthracene; so unstable are the bromine additive compounds of these hydrocarbons.

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* It is remarkable that all the hydrocarbons in which the carbon atoms are supposed to be united so as to form a closed chain, containing two or more loops united together at *two* points, such as naphthalene, fluorene, acenaphthene, anthracene, phenanthrene, pyrene, chrysene, and dinaphthylmethane, combine with trinitrophenol, and that this combination does not occur in the case of hydrocarbons such as diphenyl, in which there are also two loops, but united only at *one* point. It is noteworthy, moreover, that additive compounds have not yet been obtained from diphenyl and dinaphthyl, although from Schultz's experiments it appears probable that the action of bromine on the former does lead to the formation of an additive compound.

If the hydrocarbons of the olefine and acetylene series, valylene, and dipropargyl, are compared together merely with reference to their behaviour with bromine, it is evident that they are strictly isologous with the paraffins, since they combine with an amount of bromine which is the equivalent of the hydrogen withdrawn in their formation from the paraffins. This relation does not obtain, however, in the case of any of the remaining series of isologous hydrocarbons, from which it is inferred that the carbon atoms in them are not united in such a manner as to form an open chain. The question now arises whether it is possible to obtain hydrocarbons of the C_nH_{2n-8} and higher series, having the carbon atoms united so as to form an open chain? Direct experiments bearing upon this question have not as yet been made, but it is not improbable that the results would be negative. A somewhat similar question, and one which is of some interest, is whether a $C_{10}H_{16}$ hydrocarbon isomeric with the terpenes, and possessed of properties which would justify its ranking as a true homologue of valylene, can exist? Our present knowledge almost warrants the conclusion that such a hydrocarbon, even if capable of existing, would be extremely unstable, and that it would be readily convertible into a terpene; for the $C_{10}H_{16}$ hydrocarbon obtained from diamylene (1264) has the properties characteristic of the terpenes.

Another allied subject requiring discussion is the composition of the first or lowest term of each of the series of isologous hydrocarbons. The lowest term of the paraffin or C_nH_{2n+2} series is methane, CH_4, but the first term of the olefine or C_nH_{2n} series is ethylene, C_2H_4. Numerous experiments have been made with the object of obtaining the hydrocarbon CH_2, which have all resulted in the formation of C_2H_4, and it appears to be almost beyond question that the lowest term of the olefine series which can exist must contain two atoms of carbon. The same is undoubtedly true of the C_nH_{2n-2} series, acetylene being the lowest possible term of the series. With regard to the least number of carbon atoms which may be associated with hydrogen in the proportions necessary to form lower homologues of valylene* and dipropargyl, we have no means at present of judging; but it is difficult to resist the impression that, as the series of isologous hydrocarbons is descended, and the proportion of hydrogen to carbon diminishes, the number of carbon atoms contained in the first term of each series becomes greater and greater.

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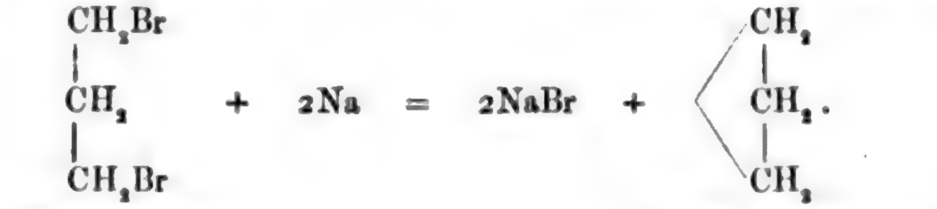
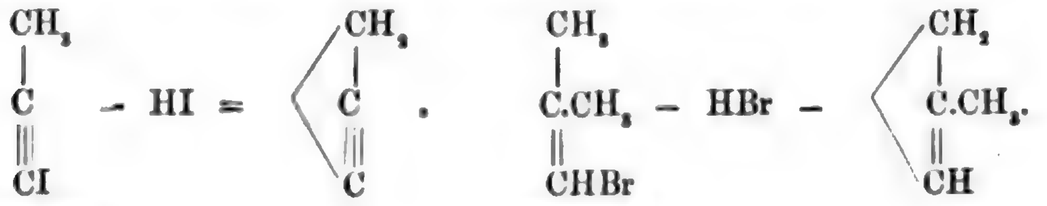
* Experiments have recently been made (Ador and Rilliet, *Deut. chem. Ges. Ber.*, viii. 1286), but with no very definite amount of success, to obtain derivatives of the additive compound $C_6H_6Br_2$, by adding first a small quantity of bromine to a relatively very large quantity of benzene, exposing the well-cooled mixture to sunlight, and then acting on the product with zincic ethide: the resulting mixture of hydrocarbons was afterwards submitted to oxidation. The acids obtained in this way were benzoic, para- and metabromobenzoic, isophthalic and terephthalic acids.

There is also very little evidence to show how few carbon atoms can be united together so as to form a closed chain, and whether, as appears probable, benzene is the simplest possible instance of this kind. There are, however, as Meyer has pointed out (*Ann. Chem. Pharm.*, clxxx. 192), a considerable number of facts which tend to prove that a closed chain cannot be formed from three carbon atoms. Thus it might be expected that α-dibromopropane (1189), when heated with metallic sodium, would furnish a hydrocarbon, C_3H_6, in which the carbon atoms are united in a closed chain, as represented by the following equation:



α-Dibromopropane. Isomeride of propylene.

It has been found, however, that the reaction does not take place in this manner, ordinary propylene, $H_2C=CH.CH_3$, being produced. Examples which are more to the purpose are afforded by the behaviour of bromisobutylene and iodallylene towards alkalies. If the elements of a molecule of haloid acid were withdrawn from each of these compounds, hydrocarbons containing three atoms of carbon united in a closed chain would result, thus:



Iodallylene. Bromisobutylene.

Iodallylene, however, is not in the least affected, even when heated with sodic ethylate; and bromisobutylene, which is not attacked by an aqueous solution of potassic hydrate, is converted into the ether, $C_4H_7.OC_2H_5$, by the action of an

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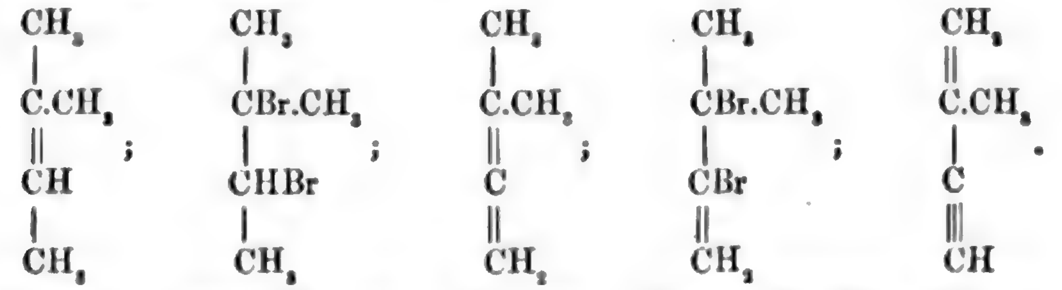
* The constitution of valylene has not been determined, but it is probable that the several stages of its formation from amylene are correctly represented by the following formulæ:



$$\begin{array}{c} CH_3 \\ | \\ C.CH_3 \\ \| \\ CH \\ | \\ CH_3 \end{array}; \quad \begin{array}{c} CH_3 \\ | \\ CBr.CH_3 \\ | \\ CHBr \\ | \\ CH_3 \end{array}; \quad \begin{array}{c} CH_3 \\ | \\ C.CH_3 \\ \| \\ C \\ \| \\ CH_2 \end{array}; \quad \begin{array}{c} CH_3 \\ | \\ CBr.CH_3 \\ | \\ CBr \\ \| \\ CH_2 \end{array}; \quad \begin{array}{c} CH_2 \\ \| \\ C.CH_3 \\ | \\ C \\ ||| \\ CH \end{array}.$$

Amylene. Amylene dibromide. Valerylene. Valerylene dibromide. Valylene.

alcoholic solution, and does not furnish a hydrocarbon even when heated with solid potassic hydrate.*

From these few observations it will be evident how much remains unknown with regard to the hydrocarbons, and how difficult it is, therefore, to institute a satisfactory comparison between the various isologous series.

The foregoing remarks have dealt chiefly with the relations of the various series of isologous hydrocarbons as exhibited by their behaviour with chlorine and bromine, but it is interesting also to compare them with reference to their behaviour with other reagents, such as concentrated nitric and sulphuric acids, and on oxidation. The paraffins resist the action of these acids, and do not furnish substitution or additive compounds with them similar to those obtained from other hydrocarbons; the olefines and acetylenes combine directly with sulphuric acid, and also, in most cases, are readily polymerized by this acid, but they do not yield characteristic products when submitted to the action of concentrated nitric acid. The terpenes, or $C_{10}H_{16}$ hydrocarbons, appear to combine with sulphuric acid, but the resulting compounds are excessively unstable, and, therefore, by the action of this reagent they are usually polymerized; they are violently attacked by strong nitric acid, but do not yield characteristic products. Benzene and its homologues, and most of the hydrocarbons of the remaining isologous series, yield substitution derivatives when submitted to the action of concentrated sulphuric or nitric acid, one or more atoms of hydrogen being displaced by the corresponding number of SO_3H or NO_2 groups; in all these hydrocarbons, it is assumed, as we have seen, that the carbon atoms, in part at least, are united so as to form a closed chain; it is noteworthy, moreover, that the hydrogen atoms which are displaced are always attached to carbon atoms which form part of the closed chain.

By prolonged treatment with oxidizing agents, the paraffins are converted into mixtures of acids of the acetic and succinic series, and similar products are obtained from the olefines, which, however, are far more readily attacked; the law of oxidation of these series of hydrocarbons has not been ascertained: it is only known that the products usually contain fewer atoms of carbon than the hydrocarbon oxidized. Little is known of the manner in which the hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series behave on oxidation, but the investigation of the terpenes in this direction appears to promise results of considerable interest and importance. Benzene, as we have seen, is entirely broken up on oxidation, but its homologues behave differently: the closed chain or C_6 group remaining intact, whilst the side chains or paraffin residues are so oxidized that only the atom or atoms of carbon which are directly united to the closed chain in the original hydrocarbon remain in union with it in the oxidation product. The hydrocarbons of the remaining series exhibit a similar behaviour. Those in which all the carbon atoms together form a closed chain, having two or more loops united together at two points, yield quinones on oxidation; these are formed from the hydrocarbon by the displacement of two atoms of hydrogen by two of oxygen, and in their properties closely resemble quinone, $C_6H_4O_2$, which is similarly related to benzene although it has not been obtained from it directly by oxidation, probably by reason of the very slight resistance which it itself opposes to oxidation. Those, on the other hand, in which the carbon atoms are partially united in a closed chain, and partially form an open chain, behave like the benzene homologues, the closed chain usually remaining intact, and the atom or atoms of carbon directly associated with it in the hydrocarbon alone remaining united to it in the oxidation product.

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* Some time since Pinner stated that the hydrocarbon C_3H_2 was produced by the action of sodium on the so-called dichlorallylene from "croton chloral." This "croton chloral" is produced by the action of chlorine on acetaldehyde, and was supposed to be a trichlorocrotonic aldehyde of the formula $C_3H_2Cl_3.COH$, "dichlorallylene," $C_3H_2Cl_2$, being formed from it by the action of alkalies. Pinner has recently admitted, however, that "croton chloral," and all the compounds derived from it, contain two atoms of hydrogen *more* than he originally stated, it being trichlorobutyric aldehyde, the hydrocarbon C_3H_2 being in reality allylene, C_3H_4. The chlorobromo*propylene* derivatives described on p. 206 are consequently *propane* derivatives.

It is noteworthy that the action of oxidizing agents upon the hydrocarbons differs greatly from that of chlorine and bromine, since carbon atoms united only by a single affinity to each other are thereby frequently disunited; in these cases, however, there appears always to be an accumulation of the negative element (oxygen) at the point of rupture previous to its occurrence: dibenzyl, $C_6H_5.CH_2.CH_2.C_6H_5$, for example, being doubtless converted into the ketone dibenzoyl, $C_6H_5.CO.CO.C_6H_5$, before it is resolved into two molecules of benzoic acid.

Hitherto the nature of the differences which exist between the various series of isologous hydrocarbons have been chiefly considered, but it is to be noticed that there is also a progressive alteration in properties in the case of the successive terms of each homologous series. The lowest and least complex members of a series are invariably the most stable, and the stability diminishes progressively as the series is ascended; moreover, the lowest members are least readily acted upon, and their derivatives are more stable than those of the succeeding terms. Thus, in the case of the paraffins, the action of chlorine appears to take place more readily, the greater the number of carbon atoms; and the same relation obtains, but is much more marked, in the case of benzene and its homologues: on the other hand, the mono-haloid derivatives of methane and ethane when submitted to the action of alkalies, lose haloid acid only at a high temperature, whereas those of the succeeding homologues are converted into olefines with increasing facility as the series is ascended. Again, the olefines appear to combine with the halogens the more readily the more complex they are, but the resulting compounds are the more stable the fewer the carbon atoms they contain. The same is true with regard to the behaviour of homologous hydrocarbons with oxidizing agents: oxidation being, as a rule, effected the more readily the more complex the hydrocarbon. It is necessary to remember, however, that owing to the occurrence of isomerism, all the members of an homologous series are not strictly comparable; the several terms in an isomeric series of hydrocarbons may differ greatly in properties, and therefore in order to ascertain the true relations of homologues, and the effect of a repetition of a similar alteration in composition, it is necessary to compare together only those homologues which occupy similar positions in the isomeric series to which they respectively belong.

It has been pointed out above that the paraffins, olefines, acetylenes, valylene, and dipropargyl may be regarded as terms in a series of strictly homologous hydrocarbons; the carbon atoms in these hydrocarbons being always united in the form of an open chain. There is little doubt that the generation of the olefines by the withdrawal of a molecule of haloid acid from the monohaloid derivatives of the paraffins, and of the acetylenes from the monohaloid derivatives of the olefines, takes place in accordance with a law which is probably of general application in all cases of withdrawal of haloid acid from haloid derivatives. Sufficient material has already been accumulated to enable us to define with considerable probability the nature of this law. It is requisite, in the first place, to bear in mind that in all the olefines two of the carbon atoms are united by two affinities of each, so that they are necessarily contiguous: this is a necessary inference from the proof above given that carbon atoms which are only united by single affinities are not disunited by the action of bromine, and that consequently the carbon atoms in the olefines do not form a closed chain, which is the only alternative if it be not admitted that two of them are united by two affinities of each. In the formation of the olefines, therefore, from the monohaloid paraffins, the atom of halogen and an atom of hydrogen which are attached to contiguous carbon atoms are withdrawn. If now we regard the formation of the *three* butylenes from the *four* iodotetranes or butylic iodides, as represented by the following equations:

$$\underset{\text{Primary butylic iodide.}}{CH_3.CH_2.CH_2.CH_2I} - HI = \underset{\text{Ethylethylene.}}{CH_3.CH_2.CH{=}CH_2},$$

$$\underset{\text{Secondary butylic iodide.}}{CH_3.CH_2.CHI.CH_3} - HI = \underset{\alpha\text{-Dimethylethylene.}}{CH_3.CH{=}CH.CH_3},$$

$$\left.\begin{array}{c} (CH_3)_2CH.CH_2I \\ \text{Isoprimary butylic iodide.} \\ \\ (CH_3)_3CI \\ \text{Tertiary butylic iodide.} \end{array}\right\} - HI = \underset{\beta\text{-Dimethylethylene.}}{(CH_3)_2C{=}CH_2},$$

and of heptylene from the iodide of dimethylisobutylcarbinol:

$$\underset{\text{Dimethylisobutylcarbylic iodide.}}{(CH_3)_2CI.CH_2.CH(CH_3)_2} - HI = \underset{\text{Isopropyldimethylethylene.}}{(CH_3)_2C{=}CH.CH(CH_3)_2},$$

it is evident that the hydrogen is always withdrawn from the *least hydrogenized* carbon atom contiguous to that to which the halogen is attached. This rule appears to be of general application,* it is not, however, a guide in the case of the formation of the olefines from the alcohols by the action of dehydrating agents, such as zincic chloride; since, as Flavitzsky's experiments have conclusively proved (*ibid.* p. 340), the amylene thus prepared from isoprimary amylic alcohol, $CH_2(OH).CH_2.CH(CH_3)_2$, is a trimethylethylene, $CH_3.HC{=}C(CH_3)_2$. But, as already pointed out (p. 194), the reaction in the latter case gives rise to a very complex product, and the occurrence of isomeric change is therefore by no means surprising. The formation of trimethylethylene in this manner, however, is of considerable interest as an illustration of the tendency which appears very generally to exist for isomeric change to occur whenever there is a possibility of the production of new methyl groups in a compound.

If we now turn to the formation of the acetylenes from the dihaloid paraffins and monohaloid olefines, we find that the law above enunciated equally obtains. The formation of the monohaloid olefines from the dihaloid paraffins differs, however, somewhat from that of the olefines from the monohaloid paraffins, since according to our present knowledge, there appears to be no tendency in the latter case for all the *possible* products to be formed: secondary butylic iodide, $CH_3.CH_2.CHI.CH_3$, for example, yielding only α-dimethylethylene, and not a mixture of it with ethylethylene; whereas two of the possible products are (probably always) obtained from the dihaloid paraffins. Thus β-dichloropropane or propylenic chloride, $CH_3.CHCl.CH_2Cl$, furnishes both β-chloropropylene, $CH_3.CH{=}CHCl$, and γ-chloropropylene, $CH_3.CCl{=}CH_2$, on treatment with potassic hydrate; it is interesting to note, however, that the third possible isomeride, α-chloropropylene, $CH_2{=}CH.CH_2Cl$, the formation of which involves the greatest departure from the law which obtains in the case of the olefines, is not produced. Moreover, the monohaloid olefine which should be formed according to the law enunciated for the olefines generally appears to be the chief product; although this probably depends much on the conditions of experiment, since γ-trichloropropane, $CH_3.CCl_2.CH_2Cl$, furnishes a mixture of β-dichloropropylene, $CH_2{=}CCl.CH_2Cl$, and δ-dichloropropylene, $CH_3.CCl{=}CHCl$, when treated with water or with potassic hydrate, the latter being chiefly produced when potassic hydrate is employed and the former when water is the agent (p. 205).

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* In describing the olefines, the butylene from secondary butylic iodide was represented as a dimethylethylene of the formula $CH_3.HC{=}CH.CH_3$, and it was pointed out that the hexylene from mannite was probably a propylmethylethylene of the formula $CH_3.HC{=}CH.C_3H_7{}^{\alpha}$. Since then Saytzeff's investigation of the olefines from normal butylic alcohol and diethylcarbinol has been published (*Ann. Chem. Pharm.*, clxxix. 296), and the results he obtains entirely confirm our views with regard to the nature of the olefines from secondary butylic and hexylic iodides. Probably also the octylene from normal secondary octylic aldehyde is not hexylethylene, but amylmethylethylene, $CH_3.HC{=}CH.C_5H_{11}{}^{\alpha}$.—Eds.

The formation of the acetylenes from the monohaloid paraffins takes place, in many cases at least, in accordance with the law which governs the production of the olefines, but hitherto very little has been done towards ascertaining their constitution. The production of acetylenes capable of forming metallic derivatives, and containing therefore, we assume, the $\equiv CH$ group, from the dichlorinated paraffins formed by displacing an atom of oxygen in the aldehydes of the formula $C_nH_{2n+1}.CH_2.COH$ by two atoms of chlorine (p. 216), is entirely in accordance with this assumption, thus:

$$\underset{\text{Dihaloid paraffin.}}{C_nH_{2n+1}.CH_2.CHCl_2} = \underset{\text{Monohaloid olefine.}}{C_nH_{2n+1}CH{=}CHCl} + HCl$$

$$\underset{\text{Monohaloid olefine.}}{C_nH_{2n+1}.CH{=}CHCl} = \underset{\text{Acetylene.}}{C_nH_{2n+1}.C\equiv CH} + HCl$$

although the formation from methylethylketone and methylpropylketone of hydrocarbons having similar properties by a parallel reaction is contrary to the law in question:

$$\underset{\text{Dihaloid paraffin from methylethylketone.}}{CH_3.CCl_2.CH_2.CH_3} - 2HCl = \underset{\text{Ethylacetylene.}}{HC\equiv C.CH_2.CH_3}$$

$$\underset{\text{Dihaloid paraffin from methylpropylketone.}}{CH_3.CCl_2.CH_2.CH_2.CH_3} - 2HCl = \underset{\text{Propylacetylene.}}{HC\equiv C.CH_2.CH_2.CH_3}.$$

Certain of the monohaloid olefines fail to furnish corresponding acetylenes, α-bromopropylene or allylic bromide, for example, being converted by an alcoholic solution of potassic hydrate into ethylallyl ether, $C_3H_5.O.C_2H_5$, whereas its isomerides yield allylene, C_3H_4; the bromobutylene $(CH_3)_2C{=}CHBr$ as already noticed behaves similarly.

The olefines and acetylenes combine with the haloid acids, &c., according to a law just as definite as that which governs their formation. The combination of the haloid acids with the olefines appears always to take place in such a manner that the halogen attaches itself to the *least hydrogenized* carbon atom; thus the butylene ethylethylene, $H_2C{=}CH.C_2H_5$, forms with hydriodic acid secondary butylic iodide, $H_3C.CHI.C_2H_5$, and its isomeride β-dimethylethylene,

$H_2C{=}C(CH_3)_2$, is converted into tertiary butylic iodide $H_3C.CI(CH_3)_2$, whilst the amylene isopropylethylene, $H_2C{=}CH.C_3H_7{}^\beta$, furnishes the secondary iodide $H_3C.CHI.C_3H_7{}^\beta$. All these examples are illustrations of the tendency to accumulate methyl groups above alluded to. When two equally hydrogenized carbon atoms are present, as in the amylene obtained from diethylcarbinol, $H_3C.HC{=}CH.CH_2.CH_3$, and the hexylene from secondary hexylic iodide from mannite, $H_3C.HC{=}CH.C_4H_9{}^\alpha$, the halogen becomes attached to the carbon atom to which the methyl group is united: these two compounds furnishing respectively the iodides $H_3C.CHI.CH_2.CH_2.CH_3$ (Saytzeff and Wagner, *Ann. Chem. Pharm.*, clxxix. 313) and $H_3C.CHI.CH_2.C_4H_9{}^\alpha$. When no methyl group is attached to either of the carbon atoms which are united by two affinities, the halogen probably attaches itself to that with which the least complex or most stable group is united. Very little is known of the hydrocarbons of the acetylene series, but they appear to behave similarly.

When the olefines combine with the haloid acids, isomeric products are not obtained,* but the result is different when they combine with hypochlorous or sulphuric acid. Thus from Henry's and Markownikoff's experiments (*Compt. Rend.*, lxxix. 1203 and 1258; *Deut. chem. Ges. Ber.*, viii. 1468), it appears that propylene, $CH_3.HC{=}CH_2$, unites with hypochlorous acid, forming either monochlorinated primary propylic alcohol, $CH_3.CHCl.CH_2(OH)$, or monochlorinated isoprimary propylic alcohol, $CH_3.CH(OH).CH_2Cl$; and that trimethylethylene, $CH_3.HC{=}C(CH_3)_2$, may form with sulphuric acid, either the compound $CH_3.H_2C.C(HSO_4)(CH_3)_2$ or $CH_3.CH(HSO_4).CH(CH_3)_2$: the former being produced under the influence of a more concentrated acid than the latter (*ibid.* viii. 1240). The different behaviour of the haloid acids, and of hypochlorous and sulphuric acids, is in a measure explicable when it is remembered that in the haloid acids the powerfully negative halogen is associated with the positive hydrogen, whereas we may regard hypochlorous acid as formed of the two radicles OH and Cl, both of which are negative; and in sulphuric acid, the group SO_4H is far less negative relatively to the remaining atom of hydrogen, than is the halogen in the haloid acids to the hydrogen associated with it.

The combination of the haloid olefines with the haloid acids, however, often results in the formation of isomeric bodies. Thus bromethylene, $H_2C{=}CHBr$, furnishes a mixture of the two dibromethanes, $CH_3.CHBr_2$ and $CH_2Br.CH_2Br$, and many similar instances might be quoted. The relative proportions of the isomerides produced appears to be entirely dependent upon conditions of experiment, just as in the case of the simultaneous formation of isomeric monohaloid derivatives of the olefines from the dihaloid paraffins. Thus α-bromopropylene or allylic bromide, $H_2C{=}CH.CH_2Br$, is almost completely converted into α-dibromopropane, $CH_2Br.CH_2.CH_2Br$, by heating with a saturated solution of hydrobromic acid, but if a less concentrated acid be employed, more or less β-dibromopropane, $CH_3.CHBr.CH_2Br$, is formed.

Lastly, it is important to compare the behaviour of the hydrocarbons of the various series with chlorine, bromine, nitric acid, &c., with reference to the constitution of the substitution derivatives which are thus formed. Unfortunately, except in the benzene series, very little systematic research has been executed with the view to ascertain the laws which govern substitution. We owe to Schorlemmer the important discovery that two isomeric monochlorinated paraffins are simultaneously generated by the action of chlorine on the *normal* paraffins; but little, however, is known of the isomeric paraffins, and it is merely probable that many of them behave similarly. The two monochlorinated normal paraffins are, it would seem, always formed by the displacement of an atom of hydrogen either in the CH_3 group or in the CH_2 group with which the CH_3 group is associated. Our knowledge of the further action of chlorine is extremely unsatisfactory. In the case of ethane, the tendency is for the atoms of hydrogen attached to the one atom of carbon to be displaced before those attached to the other are affected, although there is reason to believe that α-dichlorethane or ethylene chloride, $CH_2Cl.CH_2Cl$, is formed together with β-dichlorethane or ethylidene chloride, $CH_3.CH_2Cl_2$, by the action of chlorine on chlorethane (p. 200), especially as bromethane is known to furnish the two isomeric dibromethanes when heated with bromine (Tawildarow, *Ann. Chem. Pharm.*, clxxvi. 12). The only other reliable observations bearing upon this question in the case of the paraffins, are those of Friedel and Silva, according to whom both α- and β-chloropropane, $CH_3.CH_2.CH_2Cl$ and $CH_3.CHCl.CH_3$, furnish β-dichloropropane, $CH_3.CHCl.CH_2Cl$, the latter also yielding δ-dichloropropane, $CH_3.CCl_2.CH_3$; whilst β-dichloropropane is converted into a mixture of α-trichloropropane, $CH_2Cl.CHCl.CH_2Cl$, and β-trichloropropane, $CH_3.CHCl.CHCl_2$, by heating with iodine chloride. It is difficult, therefore, in the case of the paraffins, to say whether an atom of chlorine or bromine associated with a carbon atom tends to attract a second atom of chlorine or bromine to, or to repel it from, the same carbon atom.

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* It is not improbable that the higher olefines will be found to furnish isomeric compounds with the haloid acids, and similarly the higher monohaloid paraffins to furnish isomeric olefines.

The nature of the action of the halogens, &c., on benzene and its homologues has been already very fully discussed. It is only necessary to recall the fact that in the case of the halogens, the tendency is always to produce the para- or 1 : 4 di-derivative and a variable amount of the ortho- or 1 : 2 di-derivative; by the continued action of the halogen, the 1 : 2 : 4 tri-derivative appears to be the main if not the sole product formed from the para- meta- and ortho- di-derivatives. There is also the same tendency to produce a para- and ortho- di-derivative when nitric or sulphuric acid acts on a monohaloid derivative of benzene, and to form a 1 : 2 : 4 tri-derivative when they act upon the di-haloid derivative: in fact, under all circumstances the 1 : 2 : 4 tri-derivatives are produced in preference. Finally, it is to be noticed that the formation of substitution derivatives from the hydrocarbons isologous with benzene by the displacement of hydrogen atoms attached to the carbon atoms which are united in a closed chain, to judge from the relatively small amount of evidence at our disposal, appears to take place in a manner precisely similar to that observed in the case of benzene; para- and ortho- di-derivatives being formed by the action of the halogens, and meta- di-derivatives being seldom produced except by the agency of nitric and sulphuric acid. In fact, substitution generally, including such cases as the formation of the benzylbenzenes, benzyltoluenes, and phenanthrene, appears to be regulated by similar laws.

CHAPTER VI.

THE ALCOHOLS.

§ I. *Alcohols of the* $C_nH_{2n+1}.OH$ *or ethylic series*;—§ II. *Alcohols of the* $C_nH_{2n-1}.OH$ *or allylic series*;—§ III. *Alcohols of the* $C_nH_{2n-3}.OH$ *and* $C_nH_{2n-5}.OH$ *series*;—§ IV. *Alcohols of the* $C_nH_{2n-7}.OH$ *series*;—§ V. *Monohydric alcohols derived from the hydrocarbons isologous with benzene*;—§ VI. *Alcohols of the* $C_nH_{2n}(OH)_2$ *or glycolic series*;—§ VII. *Alcohols of the* $C_nH_{2n-8}(OH)_2$ *series*;—§ VIII. *Dihydric alcohols of other series*;—§ IX. *Alcohols of the* $C_nH_{2n-1}(OH)_3$ *series*;—§ X. *Alcohols of the* $C_nH_{2n-9}(OH)_3$ *series*;—§ XI. *Alcohols of the* $C_nH_{2n-2}(OH)_4$ *series*;—§ XII. *Alcohols of the* $C_nH_{2n-3}(OH)_5$ *series*;—§ XIII. *Alcohols of the* $C_nH_{2n-4}(OH)_6$ *series, the glucoses, sucroses, and amyloses*;—§ XIV. *Thioalcohols of various series.*

(1417) *General Character of the Alcohols.*—The term alcohol is of Arabic origin, and was originally applied specifically to the volatile inflammable spirituous liquid which is the characteristic product of the fermentation of sugar; since then, however, it has been made generic, and extended to a class of bodies which, for the most part, possess qualities more or less analogous to those of spirit of wine or ethylic alcohol.

The term alcohol has recently received a still further extension of meaning, and is now generally applied to all those compounds of carbon, oxygen, and hydrogen, which may be regarded as derived from a hydrocarbon by the displacement of one or more hydrogen atoms, by an equal number of the monad group OH: thus including such substances as glycerin, mannite, phenol, benzhydrol, orcin, and pyrogallol; and it is in this extended signification that the term alcohol will be employed in this volume.

It is evident that not only will each series of isologous hydrocarbons be capable of giving rise to a corresponding series of alcohols, but that the same hydrocarbon may give rise to alcohols of a different class, according as one, two, three, or more hydrogen atoms are displaced by one, two, three, or more OH groups. For instance, not only do the isologous hydrocarbons hexane, C_6H_{14}, and benzene, C_6H_6, give rise to the alcohols $C_6H_{13}.OH$ (hexylic alcohol) and $C_6H_5.OH$ (phenol), but the same hydrocarbon benzene yields phenol, $C_6H_5.OH$, resorcin, $C_6H_4(OH)_2$, and pyrogallol, $C_6H_3(OH)_3$, all of which come under the definition of alcohols. In order to distinguish the alcohols containing one OH group from those which contain two, the former are called *monohydric* alcohols, and the latter *dihydric*; the terms *trihydric*, *tetrahydric*, &c., being similarly employed to designate those which contain three, four, or more OH groups.*

It is important to notice that the number of polyhydric alcohols which may be obtained from any hydrocarbon is apparently limited by the number of carbon atoms it contains, for it has been found that each carbon atom never unites *with more than one OH group* to form a *stable* combination;† thus, although methane, CH_4, can yield a monohydric alcohol, $CH_3.OH$, no corresponding dihydric alcohol, $CH_2(OH)_2$, has been isolated; from ethane, C_2H_6, a monohydric alcohol, $C_2H_5.OH$, can be obtained, and also a dihydric alcohol, $C_2H_4(OH)_2$, but no trihydric or tetrahydric.

§ I. MONOHYDRIC ALCOHOLS OF THE $C_nH_{2n+1}.OH$ OR ETHYLIC SERIES.

(1418) This series contains by far the largest number of those alcohols which are best known and which have been most completely investigated. Their modes of formation, reactions, and chemical relations may best be illustrated by considering them as derived from the corresponding paraffins by the displacement of one atom of hydrogen by one OH group, although they may also be regarded as compounds of hydroxyl, OH, with positive monad organic radicles of the methyl series, or as water in which one atom of hydrogen has been displaced by the radicle. For instance, we may suppose ethylic alcohol, $CH_3.CH_2(OH)$ or $C_2H_5.OH$, either to be derived from ethane, $CH_3.CH_3$, by the displacement of H by OH, or to be formed by the union of the radicle ethyl, $CH_3.CH_2$ or C_2H_5, with hydroxyl, OH, or we may represent it as water, OH_2, in which H has been displaced by C_2H_5. Obviously, however, these are mere distinctions in words, and indicate no real differences.

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* The terms *monatomic*, *diatomic*, &c., have been used for the purpose of classification of the alcohols in the same sense as monohydric, dihydric, &c., but a reference to the meaning attached to the word atomic (note p. 44) will at once show the inconsistency of such a nomenclature.

† The *possibility* of the existence of compounds in which more than one OH group is directly associated with the same carbon atom is even disputed by some chemists. Many, however, contend that they are capable of existing in the presence of an excess of water; and that it is impossible to isolate them merely on account of their instability and the tendency which they exhibit to split up with elimination of the elements of a molecule of water. This subject will be more fully treated when the dihydric alcohols are discussed.

Of these alcohols the following terms are known:

Methylic alcohol	$CH_3.OH$
Ethylic "	$C_2H_5.OH$
Propylic "	$C_3H_7.OH$
Butylic or tetrylic alcohol	$C_4H_9.OH$
Pentylic or amylic "	$C_5H_{11}.OH$
Hexylic alcohol	$C_6H_{13}.OH$
Heptylic "	$C_7H_{15}.OH$
Octylic "	$C_8H_{17}.OH$
Nonylic "	$C_9H_{19}.OH$
Cetylic "	$C_{16}H_{33}.OH$
Cerotic or cerylic	$C_{27}H_{55}.OH$
Melissic "	$C_{30}H_{61}.OH$

(1419) *Classification.*—The ethylic series of monhydric alcohols comprises a large number of isomerides, which may be conveniently arranged in three great groups of *primary*, *secondary*, and *tertiary* alcohols; these being again divisible into sub-groups. The members of each of these three groups are especially characterized and distinguished the one from the other by their behaviour on oxidation. Moreover, the boiling points of any one of the primary alcohols is always higher than that of the corresponding secondary alcohol, and the latter, again, higher than that of the corresponding tertiary alcohol.

Kolbe was the first to apply a systematic classification to the alcohols, giving them the generic name of *carbinols*. In his system, the first term of the series, methylic alcohol, $CH_3.OH$, is called carbinol, and all the homologous alcohols are regarded as derived from it by the displacement of one or more of the three hydrogen atoms of the CH_3 group by monad radicles of the form C_nH_{2n+1}; thus ethylic alcohol is *methyl carbinol*, $CH_2(CH_3).OH$, being derived from carbinol, $CH_3.OH$, by the displacement of one of the hydrogen atoms by CH_3; normal propylic alcohol again is *ethyl carbinol*, $CH_2(C_2H_5).OH$, whilst the isomeric isopropylic alcohol is *dimethyl carbinol*, $CH(CH_3)_2.OH$. Those alcohols which, from their manner of formation or the reactions they exhibit, may be regarded as derivatives of carbinol in which only a single hydrogen atom in the CH_3 group is displaced by a C_nH_{2n+1} radicle are termed *primary* alcohols; whilst, if two atoms of hydrogen are displaced by radicles of the general form C_nH_{2n+1}, the alcohol is a *secondary* alcohol; and in a similar manner those in which all three are displaced are called *tertiary* alcohols. The three groups of primary, secondary, and tertiary alcohols may therefore be represented by the following general formulæ, $CH_3.OH$ being that of methylic alcohol or carbinol itself:

$$\underset{\text{Primary carbinol.}}{CH_2(C_nH_{2n+1}).OH}\ ,\quad \underset{\text{Secondary carbinol.}}{CH(C_nH_{2n+1})_2.OH}\ ,\quad \underset{\text{Tertiary carbinol.}}{C(C_nH_{2n+1})_3.OH.}$$

It should be observed, however, that in a secondary alcohol it is not necessary that both the monad radicles represented by the general formula C_nH_{2n+1} should be the same; for instance, one of the groups may be methyl, and the other ethyl, giving rise to the secondary alcohol, methylethyl carbinol, $CH(CH_3)(C_2H_5).OH$. This remark applies with equal force to the tertiary alcohols, although as yet no alcohols have been prepared containing more than two different radicles.

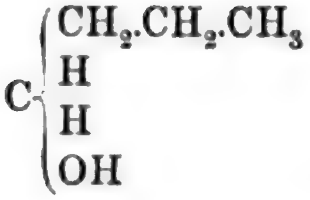
(1420) *Isomerism of the Alcohols of the Ethylic Series.*—As there is every reason for believing that the three hydrogen atoms of the methyl group in carbinol are of equal value, only one ethylic alcohol can exist; this is derived from carbinol by the displacement of one atom of hydrogen by methyl:

$$\underset{\text{Carbinol.}}{CH_3.OH} \qquad \underset{\text{Methyl carbinol.}}{CH_3.CH_2.OH.}$$

Of the next term of the series, however, propylic alcohol, two isomerides are possible; one formed by the displacement of *one* atom of hydrogen in carbinol by ethyl, the other by the displacement of *two* hydrogen atoms by two methyl groups:

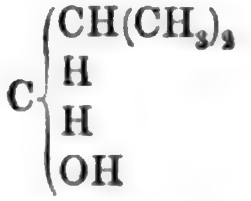
$$\underset{\text{Ethyl carbinol.}}{C_2H_5.CH_2.OH} \qquad \underset{\text{Dimethyl carbinol.}}{(CH_3)_2CH.OH.}$$

As the series of alcohols is ascended, the number of possible isomeric modifications increases very rapidly; thus the alcohol $C_4H_9.OH$ (butylic alcohol) admits of four different modifications, all of which have been obtained; they may be considered as derived from carbinol in the manner indicated by the following formulæ:



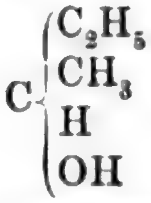
$$C\left\{\begin{array}{l}CH_2.CH_2.CH_3\\H\\H\\OH\end{array}\right.$$

Propyl carbinol.



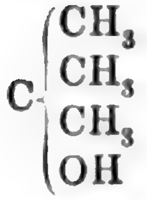
$$C\left\{\begin{array}{l}CH(CH_3)_2\\H\\H\\OH\end{array}\right.$$

Isopropyl carbinol.



$$C\left\{\begin{array}{l}C_2H_5\\CH_3\\H\\OH\end{array}\right.$$

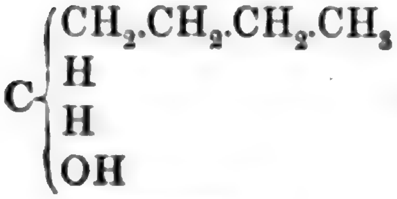
Ethyl methyl carbinol.



$$C\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\\OH\end{array}\right.$$

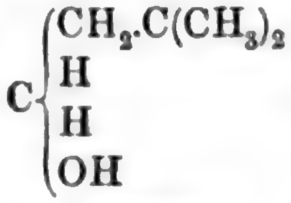
Trimethyl carbinol.

Two of these, it will be seen, are primary alcohols; one is a secondary, and one a tertiary alcohol. If we suppose the group OH removed from each of these formulæ, *four* isomeric monad hydrocarbon groups (butyls) remain—namely, $CH_2.CH_2.CH_2.CH_3$, $CH_2.CH(CH_3)_2$, $CH(CH_3)(C_2H_5)$, and $C(CH_3)_3$—and by introducing these into carbinol in place of one atom of hydrogen, four isomeric primary butylcarbinols, or amylic alcohols, will be obtained; in addition to which three isomeric secondary, and one tertiary, amylic alcohol are possible:



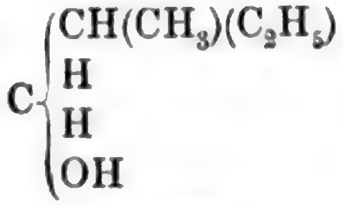
$$C\left\{\begin{array}{l}CH_2.CH_2.CH_2.CH_3\\H\\H\\OH\end{array}\right.$$

Primary-butyl carbinol.



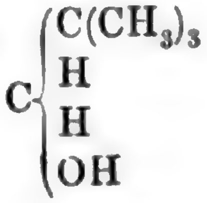
$$C\left\{\begin{array}{l}CH_2.C(CH_3)_2\\H\\H\\OH\end{array}\right.$$

Isoprimary-butyl carbinol.



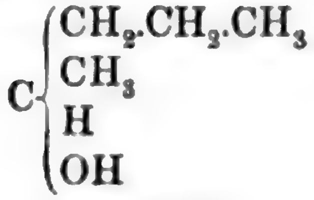
$$C\left\{\begin{array}{l}CH(CH_3)(C_2H_5)\\H\\H\\OH\end{array}\right.$$

Secondary-butyl carbinol.



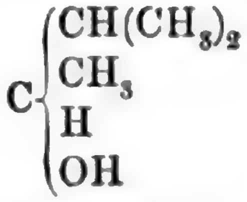
$$C\left\{\begin{array}{l}C(CH_3)_3\\H\\H\\OH\end{array}\right.$$

Tertiary-butyl carbinol.



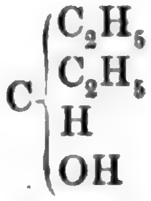
$$C\left\{\begin{array}{l}CH_2.CH_2.CH_3\\CH_3\\H\\OH\end{array}\right.$$

Primary-propyl methyl carbinol.



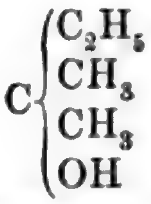
$$C\left\{\begin{array}{l}CH(CH_3)_2\\CH_3\\H\\OH\end{array}\right.$$

Isoprimary-propyl methyl carbinol.



$$C\left\{\begin{array}{l}C_2H_5\\C_2H_5\\H\\OH\end{array}\right.$$

Diethyl carbinol.



$$C\left\{\begin{array}{l}C_2H_5\\CH_3\\CH_3\\OH\end{array}\right.$$

Ethyl dimethyl carbinol.

Of these amylic alcohols seven have been already obtained. These examples will suffice to illustrate the manner in which the various isomeric alcohols are derived from, and allied to carbinol.

METHODS OF FORMATION OF THE ALCOHOLS OF THE $C_nH_{2n+1}.OH$ OR ETHYLIC SERIES.

(1421) PRIMARY ALCOHOLS: $C_nH_{2n+1}.CH_2.OH$. — Three methods of preparing these alcohols are at present known which are of general application.

1. *From Paraffins.*—It has already been noticed that when the

normal paraffins are acted on by chlorine, they furnish a mixture of two isomeric monochlorinated derivatives. One of these, that which possesses the higher boiling point, has the composition represented by the general formula, $C_nH_{2n+1}.CH_2Cl$; and by heating with argentic acetate, or a mixture of potassic acetate and glacial acetic acid, may be converted into the corresponding acetate:

$$C_nH_{2n+1}.CH_2Cl + KC_2H_3O_2 = C_nH_{2n+1}.CH_2(C_2H_3O_2) + KCl.$$

$$\underset{\text{a-Chloropropane.}}{CH_3.CH_2.CH_2Cl} + KC_2H_3O_2 = \underset{\text{Propylic acetate.}}{CH_3.CH_2.CH_2(C_2H_3O_2)} + KCl.$$

By the action of potassic hydrate solution on this acetate, potassic acetate and the normal primary alcohol are produced:

$$C_nH_{2n+1}.CH_2(C_2H_3O_2) + KHO = C_nH_{2n+1}.CH_2.OH + KC_2H_3O_2.$$

$$\underset{\text{Propylic acetate.}}{C_2H_5.CH_2(C_2H_3O_2)} + KHO = \underset{\text{Propylic alcohol.}}{C_2H_5.CH_2.OH} + KC_2H_3O_2.$$

On account of the great difficulty of separating the isomeric chloroparaffins, this method is not available for the preparation of the pure normal primary alcohols.

The *isoparaffins* also furnish two monochloroparaffins on treatment with chlorine, and that of higher boiling point may be converted in the manner above described into the corresponding isoprimary alcohol. The behaviour of other paraffins with chlorine has not been studied, but isoprimary alcohols will doubtless also be procured from many of them.

2. *From Primary Aldehydes.*—It was discovered by Wurtz that the aldehydes may be converted into the corresponding primary alcohols by means of nascent hydrogen:

$$C_nH_{2n+1}.COH + H_2 = C_nH_{2n+1}.CH_2.OH.$$

$$\underset{\text{Acetic aldehyde.}}{CH_3.COH} + H_2 = \underset{\text{Ethylic alcohol.}}{CH_3.CH_2.OH.}$$

The method usually adopted is to add sodium amalgam to a mixture of the aldehyde and water, taking care to keep the solution acid by the addition of dilute sulphuric acid from time to time. Schorlemmer recommends that the aldehyde should be dissolved in acetic acid when it is not readily soluble in water (*Ann. Chem. Pharm.*, clxxvii. 303).

In this way the *normal primary aldehydes* are converted into *normal primary alcohols*, and the isomeric aldehydes furnish isomeric primary alcohols. But the method is of great importance not only on this account, but also because it affords a means of obtaining any given alcohol from the one next below it in the series. For example, methylic alcohol, $CH_3.OH$, is converted by the action of hydriodic acid into methylic iodide or iodomethane, CH_3I, and by heating this with potassic cyanide cyanomethane, $CH_3.CN$, is produced. By digesting cyanomethane with a solution of sodic hydrate, sodic acetate is produced :

$$\underset{\text{Cyanomethane.}}{CH_3.CN} + OH_2 + NaOH = \underset{\text{Sodic acetate.}}{CH_3.COONa} + NH_3 ;$$

and when a dry mixture of sodic acetate and sodic formate is distilled, it yields acetic aldehyde :

$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + \underset{\text{Sodic formate.}}{HCOONa} = \underset{\text{Acetic aldehyde.}}{CH_3.COH} + Na_2CO_3.$$

Finally, ethylic alcohol is prepared from the aldehyde by Wurtz's method. In a similar manner, ethylic alcohol may be converted into primary propylic alcohol, and primary propylic alcohol into normal primary butylic alcohol, and thus the series of primary alcohols may be ascended.

2. *From Acid Anhydrides.*—The acid anhydrides are also converted into primary alcohols by the action of nascent hydrogen produced by carefully adding sodium amalgam to a mixture of the anhydride with the acid from which it is derived (Linnemann, *Ann. Chem. Pharm.*, clxi. 178) :

$$\left.\begin{matrix}C_nH_{2n+1}.CO\\C_nH_{2n+1}.CO\end{matrix}\right\}O + 4H_2 = 2C_nH_{2n+1}.CH_2.OH + OH_2.$$

$$\underset{\text{Butyric anhydride.}}{\left.\begin{matrix}C_3H_7.CO\\C_3H_7.CO\end{matrix}\right\}O} + 4H_2 = \underset{\text{Butylic alcohol.}}{2C_3H_7.CH_2.OH} + OH_2.$$

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A better yield of alcohol is usually obtained by a modification of this method, by the action of sodium amalgam on a mixture of the acid with its chloride (Linnemann: Saytzeff) :

$$C_nH_{2n+1}.COCl + 2H_2 = C_nH_{2n+1}.CH_2.OH + HCl.$$

$$\underset{\text{Butyric chloride.}}{C_3N_7.COCl} + 2H_2 = \underset{\text{Butylic alcohol.}}{C_3H_7.CH_2.OH} + HCl.$$

In both instances the acid serves to generate hydrogen with the amalgam, and probably both the anhydride and chloride are reduced to aldehyde previous to their conversion into alcohol. By the employment of anhydrides and chlorides derived from *normal primary acids,* normal primary alcohols are obtained, whilst those derived from isomeric acids furnish isoprimary alcohols.

Primary propylic alcohol is formed in small quantity during fermentation, and several of the normal primary alcohols occur as ethereal salts in certain vegetable products; for instance, the oil of wintergreen from the *Gaultheria procumbens* consists chiefly of *methylic* salicylate, whilst the oils from *Heracleum giganteum*, *H. spondylium*, and *Partinacea sativa* contain *ethylic* butyrate, *hexylic* butyrate, and *octylic* acetate (Gutzeit, *Ann. Chem. Pharm.*, clxx. 344). Chinese wax consists chiefly of *cerylic* cerotate, cerylic alcohol being the highest term but one of the series. The isoprimary butylic, amylic, and (probably) hexylic alcohols are constituents of the so-called fusel oil, which is the residue of high boiling point obtained on distilling the crude alcohol manufactured by fermentation.

SECONDARY ALCOHOLS: $\left.\begin{matrix}C_nH_{2n+1}\\ C_mH_{2m+1}\end{matrix}\right\}CH.OH$.—These alcohols, we have seen, may be regarded as carbinol, $CH_3.OH$, in which two atoms of hydrogen are displaced by two similar or different monad hydrocarbon radicles of the general formula C_nH_{2n+1}. If these groups are normal radicles, that is to say, if their carbon atoms are arranged in a single chain as in the normal paraffins, the alcohols are termed normal secondary alcohols; and when this is not the case they are termed isosecondary alcohols. Several general methods of preparation are known.

1. *From Paraffins.*—The chloroparaffins of lower boiling point produced by the action of chlorine on the normal and isoparaffins may be converted into normal and isosecondary alcohols respectively, by the same series of reactions as are employed in preparing primary alcohols from the paraffins; thus:

$$\underset{\beta\text{-Chloropropane.}}{CH_3CHCl.CH_3} + KC_2H_3O_2 = \underset{\text{Isopropylic acetate.}}{CH_3.CH(C_2H_3O_2).CH_3} + KCl.$$

$$\underset{\text{Isopropylic acetate.}}{CH_3.CH(C_2H_3O_2).CH_3} + KHO = \underset{\text{Secondary propylic alcohol.}}{CH_3.CH(OH).CH_3} + KC_2H_3O_2.$$

The chloroparaffins which furnish secondary, are far less stable than those which yield primary alcohols, and a considerable amount of the corresponding olefine is usually generated together with the acetate, by the secondary reaction illustrated in the following equation:

$$\underset{\beta\text{-Chloropentane.}}{CH_3.CHCl.CH_2.C_2H_5} + KC_2H_3O_2 = \underset{\alpha\text{-Ethylmethylethylene.}}{CH_3.CH{=}CH.C_2H_5} + KCl + HC_2H_3O_2.$$

2. *From Ketones.*—The ketones of the general formula $C_nH_{2n+1}.CO.C_mH_{2m+1}$ are converted by the action of nascent

hydrogen into secondary alcohols, the reaction being precisely similar to that by which aldehydes are converted into primary alcohols:

$$C_nH_{2n+1}.CO.C_mH_{2m+1} + H_2 = C_nH_{2n+1}.CH(OH).C_mH_{2m+1}.$$

$$\underset{\text{Methylethylketone.}}{CH_3.CO.C_2H_5} + H_2 = \underset{\text{Methylethylcarbinol.}}{CH_3.CH(OH).C_2H_5.}$$

The ketones which contain normal radicles alone furnish normal alcohols, those which contain isoradicles yielding isosecondary alcohols.

3. *From Ethylic Formate and the Zinc Organo-metallic Compounds.*—Secondary alcohols are also obtained by the action of the zinc organo-metallic compounds on ethylic formate, and subsequent treatment of the product with water. The reaction probably occurs in several phases as represented by the following equations (Wagner and Saytzeff, *Ann. Chem Pharm.*, clxxv. 361):

$$\underset{\text{Ethylic formate.}}{HCO.OC_2H_5} + \underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} = HC(C_2H_5)(Zn.OC_2H_5).OC_2H_5;$$

$$HC(C_2H_5)(Zn.OC_2H_5).OC_2H_5 + Zn(C_2H_5)_2 = HC(C_2H_5)_2(Zn.OC_2H_5) + Zn\left\{\begin{matrix}OC_2H_5\\C_2H_5\end{matrix}\right.$$

$$HC(C_2H_5)_2(Zn.OC_2H_5) + 2OH_2 = \underset{\text{Diethylcarbinol.}}{HC(C_2H_5)_2.OH} + Zn(OH)_2 + C_2H_6.$$

4. *From Chlorinated Ether.*—A fourth method of preparing secondary alcohols, which appears to be of general application, consists in acting with the zinc organo-metallic compounds on the dichlorethylic ether produced by the action of hydrochloric acid on aldehyde; the ether which is thus obtained is converted into the iodoparaffin by heating with hydriodic acid solution, and from this the alcohol may be prepared (See p. 413, Kessel, *Ann. Chem. Pharm.*, clxxv. 44):

$$\underset{\text{Dichlorethylic oxide.}}{\left.\begin{matrix}CH_3.CHCl\\CH_3.CHCl\end{matrix}\right\}O} + 2Zn(C_2H_5)_2 = \underset{\text{Secondary butylic oxide.}}{\left.\begin{matrix}CH_3.CH(C_2H_5)\\CH_3.CH(C_2H_5)\end{matrix}\right\}O} + 2ZnClC_2H_5.$$

$$\underset{\text{Secondary butylic oxide.}}{\left.\begin{matrix}CH_3.CH(C_2H_5)\\CH_3.CH(C_2H_5)\end{matrix}\right\}O} + 2HI = \underset{\text{Secondary butylic iodide.}}{2CH_3.CHI.C_2H_5} + OH_2.$$

It would probably be possible to convert the ether directly into the alcohol by heating it with dilute sulphuric acid.

TERTIARY ALCOHOLS: $\left.\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}C.OH$.—Although it cannot be doubted that tertiary alcohols may exist containing three dissimilar radicles in place of the three atoms of hydrogen in the

CH_3 group in carbinol, all the alcohols at present known contain three similar, or two similar and one dissimilar, radicles. The only general method of preparing them is to act upon the chlorides of the acids of the acetic series with the zinc organo-metallic compounds, and subsequently to decompose the product with water. The manner in which the reaction takes place is not yet placed beyond doubt, but it exhibits several phases. According to Wagner and Saytzeff (*loc. cit.*) the following equations represent the changes which finally result in the formation of trimethylcarbinol, for instance, from acetic chloride and zincic methide:

$$\underset{\text{Acetic chloride.}}{CH_3.COCl} + \underset{\text{Zincic methide.}}{Zn(CH_3)_2} = CH_3.CCl(CH_3)(Zn.OCH_3).$$

The reaction represented by this equation is extremely violent, and if water is added when the acid chloride and zinc compounds are mixed in the proportions indicated, a *ketone* is obtained. The decomposition may be supposed to take place in the manner expressed by the equation:

$$CH_3.CCl(CH_3)(Zn.OCH_3) + 2OH_2 = CH_3.CCl(CH_3)(OH) + Zn(OH)_2 + CH_4;$$

the compound $CH_3.CCl(CH_3)(OH)$ splitting up into the ketone $CH_3.CO.CH_3$ and hydrochloric acid. If, however, a second molecule of the zinc compound be added, a further reaction slowly takes place, consisting probably in the displacement of the chlorine by methyl:

$$CH_3.CCl(CH_3)(Zn.OCH_3) + Zn(CH_3)_2 = CH_3.C(CH_3)_2(Zn.OCH_3) + ZnClCH_3.$$

The compound $ZnClCH_3$ appears from Butlerow's experiment, by whom this method was discovered, in some way to enter into combination with the main product of the reaction. Finally, the formation of trimethylcarbinol by the action of water on this product is represented by the following equation:

$$CH_3.C(CH_3)_2(ZnOCH_3) + 2OH_2 = C(CH_3)_3.OH + Zn(OH)_2 + CH_4.$$

On the other hand, it may be supposed that the first action of the zinc compound is to convert the acid chloride into the ketone:

$$CH_3.COCl + Zn(CH_3)_2 = CH_3.CO.CH_3 + ZnClCH_3;$$

and that then by the action of a second molecule of the zinc compound the ketone is slowly converted into the body which furnishes the alcohol on treatment with water:

$$CH_3.CO.CH_3 + Zn(CH_3)_2 = C(CH_3)_3(Zn.OCH_3).$$

This latter view is supported by the circumstance that the zinc organo-metallic compounds, $Zn(C_nH_{2n+1})_2$, react with great readiness upon haloid derivatives generally, the halogen being displaced by the hydrocarbon radicle, and that therefore it is probable that by their action upon the acid chlorides, the chlorine would be directly displaced; moreover it appears likely from the general behaviour of these zinc compounds, that in a reaction of this kind much heat would be developed, which is the case, whereas it is not probable that an action of the kind supposed to take place by Wagner and Saytzeff would be attended by the developement of a very large amount of heat.

Several other methods of preparing alcohols are known which are of considerable importance, but they are not so generally applicable; and the alcohols which they furnish are sometimes primary, sometimes secondary, and sometimes tertiary.

1. Thus alcohols may be obtained from the iodoparaffins formed by combining the olefines with hydriodic acid.

The combination appears always to take place in such a manner that the iodine attaches itself to the least hydrogenized carbon atom in the olefine, so that it is possible to predict the nature of the alcohol which will be obtained from a given olefine; and on the other hand, to infer the nature of the olefine from that of the alcohol which is obtained from it in this way. The following general equations represent the behaviour of the three classes of olefines:

$$H_2C{=}CH.C_nH_{2n+1} \; + \; HI \; = \; H_3C.CHI.C_nH_{2n+1}.$$

$$H_2C{=}C(C_nH_{2n+1})_2 \; + \; HI \; = \; H_3C.CI(C_nH_{2n+1})_2.$$

$$C_nH_{2n+1}.HC{=}CH.C_nH_{2n+1} \; + \; HI \; = \; C_nH_{2n+1}.H_2C.CHI.C_mH_{2m+1}.^*$$

The following represent special cases:

$$H_2C{=}CH.C_2H_5 \; + \; HI \; = \; H_3C.CHI.C_2H_5.$$

Normal butylene. Secondary butylic iodide.

$$H_2C{=}C(CH_3)_2 \; + \; HI \; = \; H_3C.CI(CH_3)_2.$$

Isobutylene. Tertiary butylic iodide.

$$H_3C.HC{=}CH.C_2H_5 \; + \; HI \; = \; H_3C.HCI.CH_2.C_2H_5.$$

Amylene. Secondary amylic iodide.

In order to convert the iodoparaffins thus produced into alcohols, the method of digesting them with plumbic hydrate and water, recently suggested by Flavitzky (*Ann. Chem. Pharm.*, clxxv. 380), may probably be employed with advantage:

$$2C_nH_{2n+1}I \; + \; Pb(OH)_2 \; = \; 2C_nH_{2n+1}.OH \; + \; PbI_2.$$

The iodoparaffins corresponding to the primary alcohols are but little affected on heating with water in closed vessels even at a comparatively high temperature; they are the more acted upon, however, the higher their molecular weight. The iodoparaffins corresponding to secondary alcohols are much more readily acted upon, and those corresponding to the tertiary alcohols are still more easily attacked. But the conversion into alcohol and haloid acid according to the equation:

$$C_nH_{2n+1}I \; + \; OH_2 \; = \; C_nH_{2n+1}.OH \; + \; HI,$$

is never complete owing to the occurrence of the inverse action, although it becomes the more so the greater the quantity of water employed and the higher the temperature to which the mixture is heated. When the hydriodic acid is removed from the sphere of action, as is the case when plumbic hydrate is used, the conversion into alcohol is almost complete and also takes place more readily. It is merely necessary to heat the iodoparaffin on the water bath with water and an excess of plumbic hydrate in a flask attached to a reversed condenser; the product is afterwards distilled off, and digested with a small quantity of argentic oxide in order to remove the last traces of iodine. In cases where this method is inapplicable, the iodoparaffin is converted into an ethereal salt by double decomposition with argentic or potassic acetate, and the acetate is then saponified.

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* If the two radicles in the olefines of the form $C_nH_{2n+1}.HC{=}CH.C_mH_{2m+1}$ are dissimilar and one of them is methyl, it appears from Wagner and Saytzeff's experiments (*Ann. Chem. Pharm*, clxxix. 303) that the iodine always attaches itself to the carbon atom to which the methyl group is attached.

2. The olefines are also converted into alcohols by combining them with hypochlorous acid, and submitting the resulting chlorinated alcohols in aqueous solution to the action of sodium amalgam:

$$C_nH_{2n} + Cl.OH = C_nH_{2n}Cl.OH.$$

$$C_nH_{2n}Cl.OH + H_2 = C_nH_{2n+1}.OH + HCl.$$

$$\underset{\text{Isobutylene.}}{(CH_3)_2C{=}CH_2} + Cl.OH = \underset{\text{Chlorisobutylic alcohol.}}{(CH_3)_2ClC.CH_2.OH.}$$

$$\underset{\text{Chlorisobutylic alcohol.}}{(CH_3)_2ClC.CH_2.OH} + H_2 = \underset{\text{Isobutylic alcohol.}}{(CH_3)_2HC.CH_2.OH} + HCl.$$

3. Alcohols are also produced from the olefines by combining them with sulphuric acid, and distilling the resulting acid ethereal sulphates with water:

$$C_nH_{2n} + H_2SO_4 = C_nH_{2n+1}.HSO_4;$$

$$C_nH_{2n+1}.HSO_4 + OH_2 = C_nH_{2n+1}.OH + H_2SO_4.$$

$$\underset{\text{Isobutylene.}}{(CH_3)_2C{=}CH_2} + H_2SO_4 = \underset{\text{Tertiary-butylic hydric sulphate.}}{(CH_3)_2C(HSO_4).CH_3;}$$

$$\underset{\text{Tertiary-butylic hydric sulphate.}}{(CH_3)_2C(HSO_4).CH_3} + OH_2 = \underset{\text{Tertiary-butylic alcohol.}}{(CH_3)_2C(OH).CH_3} + H_2SO_4.$$

The law which governs the union of the olefines with hypochlorous and sulphuric acids has already been discussed (p. 401).

4. Butlerow has recently shown that in contact with dilute nitric acid and a little alcohol, the olefines (like many of the $C_{10}H_{16}$ hydrocarbons) slowly unite with water to form an alcohol (*Ann. Chem. Pharm.*, clxxx. 245):*

$$C_nH_{2n} + OH_2 = C_nH_{2n+1}.OH.$$

$$\underset{\text{Isobutylene.}}{H_2C{=}C(CH_3)_2} + OH_2 = \underset{\text{Trimethylcarbinol.}}{C(CH_3)_3.OH.}$$

On neutralizing the solution and distilling, the alcohol passes over.

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* According to Le Bel (*Compt. Rend.*, lxxxi. 967), the olefines are gradually changed in contact with water alone, and heptene and its higher homologues even yield crystalline hydrates. This observation is of interest as it serves to explain the absence of olefines from natural petroleum.

5. When the nitrites of the primary monamines such as ethylamine and its homologues are gently heated in aqueous solution, they are decomposed with evolution of nitrogen and formation of the corresponding alcohols:

$$C_nH_{2n+1}.NH_3(NO_2) = C_n'H_{2n+1}.OH + N_2 + OH_2.$$

$$\underset{\text{Ethylammonic nitrite.}}{C_2H_5.NH_3(NO_2)} = \underset{\text{Ethylic alcohol.}}{C_2H_5.OH} + N_2 + OH_2.$$

This method is difficult of execution, however, and very often does not yield favourable results.

(1422) *Diagnosis of Primary, Secondary, and Tertiary Alcohols.*—The three classes of alcohols are distinguished by their behaviour on oxidation, but in order to ascertain the nature of a given alcohol by a study of its oxidation products it is necessary, as a rule, to submit the latter to examination by quantitative analysis. Meyer and Locher have shown, however, that the three classes of alcohols may be much more readily distinguished by the aid of the corresponding nitroparaffins, even when only very small quantities of material are at the disposal of the operator. The alcohol is first converted into the iodoparaffin by treatment with hydriodic acid, and the dry iodoparaffin is then added to about an equal weight of dry argentic nitrite, which has been intimately mixed with its own volume of fine white sand: the nitrite is contained in a small distillation flask provided with a side tube four or five inches long, and when the action is over, the product is distilled off by heating with a bare flame, and is received in a small test tube. The distillate is then mixed with about three times its volume of a solution of potassic nitrite in a strong solution of potassic hydrate, and, after shaking well, dilute sulphuric acid is added drop by drop. If the alcohol is a primary alcohol and a primary nitroparaffin has been produced, the liquid at once assumes an intense dark red colour (p. 167); if it is a secondary alcohol it becomes dark blue (p. 168); whilst the product from the tertiary alcohol remains colourless, nitrous acid being without action on the tertiary nitroparaffins. No more than ·5 grm. of the iodoparaffin is required to produce these reactions with perfect distinctness (*Ann. Chem. Pharm.*, clxxx. 139).

GENERAL PROPERTIES AND REACTIONS OF THE ALCOHOLS OF THE $C_nH_{2n+1}.OH$ OR ETHYLIC SERIES.

(1423) The first nine members of the series, with the exception of some of the tertiary alcohols, which are solid, are colourless liquids at the ordinary temperature: methylic, ethylic, and propylic alcohols being miscible with water in all proportions; whilst cetylic, cerylic, and melissic alcohols are crystalline solids, insoluble in water. The other terms are oily liquids, the mobility of which, and also their solubility in water, decreases as the series is ascended. Nearly all the alcohols possess characteristic odours, and are inflammable either at the ordinary temperature or when heated.

(1424) *Behaviour of the Alcohols on Oxidation.*—When strongly heated or burnt in presence of excess of oxygen, the alcohols are converted into carbonic anhydride and water, as is generally the case with carbon compounds; but when submitted to what is commonly termed "limited" or graduated oxidation (p. 71), results are obtained varying with the nature of the alcohol, which are of the greatest value, as they usually enable us to ascertain whether it is a primary, secondary, or tertiary alcohol.

Primary Alcohols.—The first action of oxidizing agents on these alcohols is to remove a molecule of hydrogen giving rise to *aldehydes* containing *the same number of carbon atoms*:

$$\underset{\text{Ethylic alcohol.}}{CH_3.CH_2.OH} + O = \underset{\text{Acetic aldehyde.}}{CH_3.COH} + OH_2.$$

These aldehydes by the further action of the oxidizing agent are then converted into *acids of the acetic series*, also containing the same number of carbon atoms as the original alcohols:

$$\underset{\text{Acetic aldehyde.}}{CH_3.COH} + O = \underset{\text{Acetic acid.}}{CH_3.COOH}.$$

In some cases a portion of the acid produced acts on unattacked alcohol giving rise to an *ethereal salt*:

$$\underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Ethylic alcohol.}}{C_2H_5.OH} = \underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + OH_2.$$

The oxidation of a primary alcohol may therefore give rise to three distinct products: an aldehyde, an acid, and an ethereal salt. The relative proportions in which these three bodies are produced is dependent upon the conditions under which the oxidation is effected: that is to say, upon the nature of the oxidizing agent, and probably also upon the nature of the alcohol itself; upon the temperature; and especially upon the concentration of the oxidizing solution.

Secondary Alcohols.—In the case of the secondary alcohols also, the oxidation occurs in two stages, but in the first, instead of an aldehyde, a *ketone* containing the same number of carbon atoms as the alcohol is produced:

$$\underset{\text{Isopropylic alcohol or Dimethylcarbinol.}}{(CH_3)_2CH.OH} + O = \underset{\text{Acetone or Dimethylketone.}}{(CH_3)_2CO} + OH_2.$$

By the continued action of the oxidizing agent, however, the ketone is converted into one or more acids of the acetic series containing a smaller number of carbon atoms; thus:

$$\underset{\text{Acetone.}}{CH_3.CO.CH_3} + 3O = \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Formic acid.}}{H.COOH}.$$

Tertiary Alcohols.—Oxidation products containing the same number of carbon atoms are never obtained from these alcohols; but in some cases a ketone with one or more acids of the acetic series, in others one or more acids of the acetic series alone, are produced. For example:

$$\underset{\text{Trimethylcarbinol.}}{C(CH_3)_3.OH} + 3O = \underset{\text{Acetone.}}{CO(CH_3)_2} + \underset{\text{Formic acid.}}{H.COOH} + OH_2.$$

$$\underset{\text{Triethylcarbinol.}}{C(C_2H_5)_3.OH} + 6O = \underset{\text{Propionic acid.}}{C_2H_5.COOH} + \underset{\text{Acetic acid.}}{2CH_3.COOH} + OH_2.$$

It will thus be seen that the three classes of alcohols behave very differently, for whilst the *primary alcohols* yield *aldehydes* containing the same number of carbon atoms, which by further oxidation are converted into acids of the acetic series, also containing the same number of carbon atoms as the original alcohols; the *secondary alcohols* yield *ketones* containing the same number of carbon atoms, but which on further oxidation furnish acids of the acetic series containing fewer carbon atoms than the original alcohols; lastly, the *tertiary alcohols* do not under any circumstances yield products containing the same number of carbon atoms.

The behaviour of the different classes of alcohols on oxidation will be better understood, however, if the changes which probably occur are considered.

It is to be noticed that the oxidation is *always* effected in presence of water: the reagent most commonly employed being a mixture of potassic dichromate, sulphuric acid, and water. There is no doubt, moreover, that the water plays an important part in the reaction, although the precise manner in which it acts is not yet understood; probably, however, the water and the "nascent" oxygen together exercise an action which is in a measure equivalent to that of hydric peroxide, and this is indicated in the following equations by printing the oxygen and water together in a bracket.

If the action of oxidizing agents on primary alcohols be represented, as it is usually, as a mere withdrawal of two atoms of hydrogen by the oxygen:

$$\underset{\text{Primary alcohol.}}{C_nH_{2n+1}.CH_2(OH)} + O = \underset{\text{Aldehyde.}}{C_nH_{2n+1}.COH} + OH_2,$$

it is difficult to understand why the atoms of hydrogen of the OH group and *one* of the atoms from the CH_2 group are withdrawn, the two atoms having apparently very dissimilar functions in the compound; and the alternative hypothesis that the two atoms of hydrogen are withdrawn from the CH_2 group, and that thereupon the O and H in the OH group become disunited, and enter into union with the carbon atom, is equally unsatisfactory. A natural interpretation of the reaction appears to be afforded, however, by the assumption that the oxygen and water *acting together* lead to the displacement of an atom of hydrogen in the CH_2 group by OH, and that the resulting "aldehyde hydrate" is afterwards resolved into aldehyde and water:

$$\underset{\text{Primary alcohol.}}{C_nH_{2n+1}.CH_2(OH)} + (O + OH_2) = \underset{\text{Aldehyde hydrate.}}{C_nH_{2n+1}.CH(OH)_2} + OH_2;$$

$$\underset{\text{Aldehyde hydrate.}}{C_nH_{2n+1}.CH(OH)_2} = OH_2 + \underset{\text{Aldehyde.}}{C_nH_{2n+1}.COH.}$$

Aldehyde hydrates, such as according to this view are supposed to be the immediate products of the oxidation of primary alcohols, are known to exist, but they are extremely unstable bodies (see Glycols, and Aldehydes of the Acetic Series); and this fact goes far towards proving the correctness of the above explanation of the manner in which the aldehydes are formed.

The conversion of the secondary alcohols into ketones is explained in a similar manner, the immediate products of oxidation being "ketone hydrates":

$$\underset{\text{Secondary alcohol.}}{\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}CH.OH} + (O + OH_2) = \underset{\text{Ketone hydrate.}}{\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}C(OH)_2} + OH_2;$$

$$\underset{\text{Ketone hydrate.}}{\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}C(OH)_2} = OH_2 + \underset{\text{Ketone.}}{\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}CO.}$$

In the case of the tertiary alcohols, however, it appears that at first *one* of the radicles is split off under the influence of the oxidizing agent, and it may be supposed is displaced by OH; and it is probable that the immediate products of oxidation are a ketone hydrate, and an alcohol of the ethylic series:

$$\underset{\text{Tertiary alcohol.}}{\left.\begin{matrix}{}^*C_nH_{2n+1}\\C_mH_{2m+1}\\C_pH_{2p+1}\end{matrix}\right\}C.OH} + (O + OH_2) = \underset{\text{Ketone hydrate.}}{\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{\quad+1}\end{matrix}\right\}C(OH)_2} + \underset{\text{Alcohol.}}{C_pH_{2p+1}.OH.}$$

The radicle C_pH_{2p+1}, thus split off, appears always to be the least stable, which is usually the most complex. It is represented as forming an alcohol, although

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[*] In this formula *n*, *m*, and *p* may have the same value, or *n* and *m* the same value but *p* be different, or each may have a different value; the formula being so written in order to include tertiary alcohols containing two or three dissimilar radicles.

alcohols are never obtained as products of the reaction, being at once further oxidized: the oxidation products of the radicle C_pH_{2p+1} may be readily inferred, however, by the aid of the rules here laid down, according as it is a primary, secondary, or tertiary radicle: that is to say, according as it may be supposed to form a primary, secondary, or tertiary alcohol when combined with OH. The ketone hydrate is converted by loss of water into a ketone. It is true that the formation of ketones has not always been observed in the oxidation of the tertiary alcohols, but this is probably because the conditions of experiment have been such that the ketone has been at once further oxidized.

The behaviour of the ketones on oxidation is very similar to that of the tertiary alcohols. One of the radicles—and if the ketone contain dissimilar radicles it is always the less stable, which is usually the more complex radicle—is split off and separately oxidized, being presumably displaced by OH; an acid of the acetic series is thus produced, and, as before, it may be supposed that the radicle which is displaced forms an alcohol:

$$\underset{\text{Ketone.}}{\left.\begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \end{matrix}\right\} CO} + (O + OH_2) = \underset{\text{Acid.}}{C_nH_{2n+1}.COOH} + \underset{\text{Alcohol.}}{C_mH_{2m+1}.OH}.$$

If the radicle which is displaced be a primary radicle, $C_nH_{2n+1}.CH_2$, it will form a primary alcohol, and this will finally be converted into an acid of the form $C_nH_{2n+1}.COOH$ on oxidation. The behaviour of ketones, and also of tertiary alcohols, containing secondary radicles, $(C_nH_{2n+1})_2CH$, or tertiary radicles, $(C_nH_{2n+1})_3C$, has not been investigated, but it is almost beyond doubt that it will be found to accord perfectly with the results already obtained, and which are expressed in the laws above given.

(1425) *Other Reactions of the Alcohols of the* $C_nH_{2n+1}(OH)$ *Series.*—1. Many of the alcohols are oxidized when heated to a high temperature with potassic hydrate, yielding a potassic salt of an acid of the acetic series, with simultaneous elimination of hydrogen:

$$C_nH_{2n+1}.CH_2(OH) + KOH = C_nH_{2n+1}.COOK + 2H_2.$$

$$\underset{\text{Ethylic alcohol.}}{CH_3.CH_2(OH)} + KOH = \underset{\text{Potassic acetate.}}{CH_3.COOK} + 2H_2.$$

The behaviour of secondary and tertiary alcohols has not been ascertained, that of primary alcohols only being known.

2. The alcohols are readily attacked by metallic sodium or potassium, with evolution of hydrogen and the formation of a metallic derivative:

$$2C_nH_{2n+1}.OH + 2Na = 2C_nH_{2n+1}.ONa + H_2.$$

$$\underset{\text{Ethylic hydrate.}}{2C_2H_5.OH} + 2Na = \underset{\text{Sodic ethylate.}}{2C_2H_5.ONa} + H_2.$$

Similar compounds are formed when potassic hydrate is dissolved in a large excess of the alcohol, and the excess distilled off: they are the more readily produced the higher the molecular weight of the alcohol:

$$C_nH_{2n+1}.OH \ + \ KOH \ = \ C_nH_{2n+1}.OK \ + \ OH_2.$$

$$\underset{\text{Butylic hydrate.}}{C_4H_9.OH} \ + \ KOH \ = \ \underset{\text{Potassic butylate.}}{C_4H_9.OK} \ + \ OH_2.$$

In this case, the water as it is formed is carried off by the vapour of the anhydrous or nearly anhydrous alcohol. It follows from this that it is very difficult or almost impossible to dehydrate an alcohol by means of metallic sodium, or of potassic or sodic hydrate, especially if it have a high boiling point.

3. The alcohols are all converted into the corresponding monohaloid paraffin derivatives by the action of the haloid acids:

$$C_nH_{2n+1}.OH \ + \ HI \ = \ C_nH_{2n+1}I \ + \ OH_2.$$

$$\underset{\text{Propylic alcohol.}}{C_3H_7.OH} \ + \ HI \ = \ \underset{\text{Iodopropane.}}{C_3H_7I} \ + \ OH_2.$$

This reaction affords the most convenient method of preparing pure monohaloid paraffin derivatives. The best plan of operating is either to saturate the alcohol, or a mixture of the alcohol and a saturated aqueous solution of the haloid acid in convenient proportions, with the gaseous haloid acid at 0° (32° F.), and to heat the mixture in closed tubes. The heat of the water bath is usually sufficient. The conversion of the alcohol into the haloid paraffin is never perfect, but appears to be the more complete the greater the proportion of haloid acid employed; the amount of haloid paraffin produced varies also with the temperature. In order to purify the product it is washed with water, then placed in contact with calcic chloride, and when dry submitted to fractional distillation.

4. The haloid phosphorus compounds act with great readiness on the alcohols in the manner represented by the following equations (see also Ethylic Alcohol, p. 430):

α. $PCl_3 \ + \ C_nH_{2n+1}.OH \ = \ PCl_2.OC_nH_{2n+1} \ + \ HCl.$

β. $PCl_2.OC_nH_{2n+1} \ + \ C_nH_{2n+1}.OH \ = \ PCl(OC_nH_{2n+1})_2 \ + \ HCl.$

γ. $PCl(OC_nH_{2n+1})_2 + \ C_nH_{2n+1}.OH \ = \ P(OC_nH_{2n+1})_3 \ + \ HCl.$*

α. $PCl_5 \ + \ C_nH_{2n+1}.OH \ = \ POCl_3 \ + \ C_nH_{2n+1}Cl \ + \ HCl.$

β. $POCl_3 \ + \ C_nH_{2n+1}.OH \ = \ POCl_2.OC_nH_{2n+1} \ + \ HCl.$

γ. $POCl_2.OC_nH_{2n+1} \ + \ C_nH_{2n+1}.OH \ = \ POCl(OC_nH_{2n+1})_2 \ + \ HCl.$

δ. $POCl(OC_nH_{2n+1})_2 \ + \ C_nH_{2n+1}.OH \ = \ PO(OC_nH_{2n+1})_3 \ + \ HCl.$

The bromine and iodine compounds appear to behave similarly, but their action has not been so thoroughly examined.

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* It is usually stated that by the action of phosphoric oxychloride and

5. Many of the organic acids, when heated with the alcohols, furnish the corresponding ethereal salts or "compound ethers":

$$C_nH_{2n+1}.OH + R'.COOH = R'.COOC_nH_{2n+1} + OH_2.$$

$$\underset{\text{Ethylic alcohol.}}{C_2H_5.OH} + \underset{\text{Acetic acid.}}{CH_3.COOH} = \underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + OH_2.$$

Nitric,* sulphuric, and phosphoric acids also readily enter into reaction with the alcohols, and especially with the lower terms of the series; as a rule the polybasic acids, both mineral and organic, yield acid salts:

$$\underset{\text{Ethylic alcohol.}}{C_2H_5.OH} + HNO_3 = \underset{\text{Ethylic nitrate.}}{C_2H_5.NO_3} + OH_2.$$

$$\underset{\text{Amylic alcohol.}}{C_5H_{11}.OH} + H_2SO_4 = \underset{\text{Amylic hydric sulphate.}}{C_5H_{11}.HSO_4} + OH_2.$$

6. By the action of phosphoric anhydride on the alcohols, ethereal salts of phosphoric acid are produced:

$$5C_nH_{2n+1}.OH + P_2O_5 = PO(OC_nH_{2n+1})_3 + PO_2H(OC_nH_{2n+1})_2 + 2OH_2.$$

$$\underset{\text{Ethylic alcohol.}}{5C_2H_5.OH} + P_2O_5 = \underset{\text{Triethylic phosphate.}}{PO(OC_2H_5)_3} + \underset{\text{Hydric diethylic phosphate.}}{PO_2H(OC_2H_5)_2} + 2OH_2.$$

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phosphorous chloride on alcohols the corresponding monohaloid paraffins and phosphoric or phosphorous acid are produced, thus:

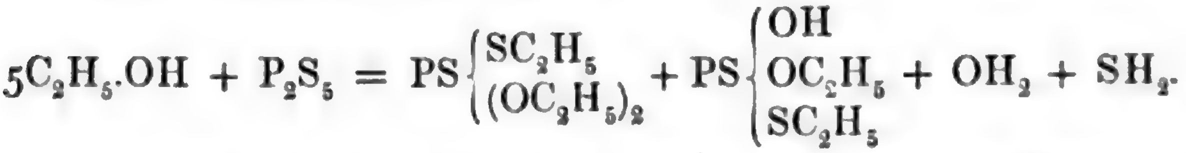
$$\underset{\text{Phosphoric oxychloride.}}{POCl_3} + \underset{\text{Alcohol.}}{3C_nH_{2n+1}.OH} = \underset{\text{Phosphoric acid.}}{PO(OH)_3} + \underset{\text{Haloid paraffin.}}{3C_nH_{2n+1}Cl};$$

$$\underset{\text{Phosphorous chloride.}}{PCl_3} + \underset{\text{Alcohol.}}{3C_nH_{2n+1}.OH} = \underset{\text{Phosphorous acid.}}{PO_3H_3} + \underset{\text{Haloid paraffin.}}{3C_nH_{2n+1}Cl};$$

and that from these acids ethereal salts are formed by the action of another portion of the alcohol. This interpretation of the reaction appears, however, to rest upon a misconception; and there is little doubt that the haloid paraffin is not the immediate product of the reaction, but that it is a secondary product formed by the action of the haloid acid produced in the manner illustrated by the above equations on a further portion of alcohol.

* When nitric acid alone is employed a portion of the acid undergoes reduction at the expense of a portion of the alcohol, and a mixed product is obtained containing, together with the nitrate, an ethereal salt of nitrous acid and oxidation products of the alcohol. By adding the alcohol to a well cooled mixture of concentrated nitric and sulphuric acid (Chapman and Smith, *Chem. Soc. Journ.*, xx. 581), or by distilling it with concentrated nitric acid and urea, the formation of these bodies is avoided; in the latter case, the nitrous acid produced by the reduction of a portion of the alcohol is decomposed by the urea.

Corresponding compounds are obtained by the action of thiophosphoric anhydride or phosphoric pentasulphide (Carius, *Ann. Chem. Pharm.*, cxix. 290); thus:



$$5C_2H_5.OH + P_2S_5 = PS\left\{\begin{matrix}SC_2H_5\\(OC_2H_5)_2\end{matrix}\right. + PS\left\{\begin{matrix}OH\\OC_2H_5\\SC_2H_5\end{matrix}\right. + OH_2 + SH_2.$$

7. By the action of various dehydrating agents, and especially of zincic chloride, the elements of a molecule of water are abstracted from the alcohols, and the corresponding olefines are formed:

$$C_nH_{2n+1}.OH = C_nH_{2n} + OH_2.$$

$$\underset{\text{Isopropylic alcohol.}}{C_3H_7.OH} = \underset{\text{Propylene.}}{C_3H_6} + OH_2.$$

Although the precise nature of the action exercised by zincic chloride upon the alcohols is not understood, it is evident from the complex character of the product in the case of amylic alcohol (p. 194) that it is far less simple than is represented by this equation, and that water is not merely abstracted.

(1426) Methylic Alcohol; *Methylic Hydrate, Wood Spirit*, or *Pyroxylic Spirit*: CH_4O or $CH_3.OH = 32$.—This alcohol, which was first observed by Taylor in 1812 amongst the products of the destructive distillation of wood, derives its name, not very appropriately, from *μέθυ*, wine. Although methylic alcohol is almost always prepared from the crude wood vinegar obtained by submitting hard woods, such as beech wood, to dry distillation at a high temperature in closed vessels, it has been obtained synthetically in several ways: from chloromethane, and from formic aldehyde* by the general methods already described, and from hydrocyanic acid by first converting it into methylamine by the action of nascent hydrogen:

$$\underset{\text{Hydrocyanic acid.}}{HCN} + 2H_2 = \underset{\text{Methylamine.}}{CH_3.NH_2};$$

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* The formic aldehyde employed for this purpose was not the pure substance, but the crude product obtained by the dry distillation of calcic formate; this was submitted to the action of sodium amalgam and water, and the alcohol isolated in the form of methylic iodide (Lieben and Rossi, *Ann. Chem. Pharm.*, clviii. 107; Linnemann and Zotta, *ibid.*, clxi. 15). Friedel and Silva have shown, however, that a certain quantity of methylic alcohol is formed on merely distilling calcic formate, and they account for its production by the supposition that the hydrogen generated by the complete decomposition of a portion of the formate acts on the aldehyde produced from another portion.

and then boiling the slightly acidulated solution of the nitrite of this base, nitrogen and water being eliminated:

$$\underset{\text{Methylamine nitrite.}}{CH_3.NH_3NO_2} = \underset{\text{Methylic alcohol.}}{CH_3(OH)} + OH_2 + N_2.$$

The methylamine obtained from any other source is equally available for the synthetical production of the alcohol. It may also be obtained by the saponification of oil of wintergreen (*Gaultheria procumbens*), or rather of the methylic salicylate, which forms the chief constituent of that essential oil:

$$\underset{\text{Methylic salicylate.}}{C_6H_4(OH).COOCH_3} + KHO = \underset{\text{Methylic alcohol.}}{CH_3(OH)} + \underset{\text{Potassic salicylate.}}{C_6H_4(OH).COOK.}$$

Preparation.—As already noticed (p. 254), the crude product of the distillation of wood is a heterogeneous mixture, of which the wood spirit forms but a very small part.

The aqueous portion after being separated from the heavier tar is rectified, and the first portions, which contain almost the whole of the methylic alcohol, are collected apart; these should be rectified from quicklime, which retains the acetic acid, the water, and most of the tarry matter. The wood naphtha of commerce, however, is often merely rectified from chalk: as thus prepared it is a mixture consisting chiefly of methylic alcohol, methylic acetate, and acetone, with oily substances insoluble in water, and which may be separated from it by admixture with water.

In order to free it from these impurities, it is mixed with an equal volume of a concentrated solution of potassic or sodic hydrate, and allowed to stand for some hours, or still better boiled with it for a time; any oily matters which may have risen to the surface after this treatment are removed, and the liquid is then distilled: the alkali decomposes the methylic acetate, usually present in large quantity, and forms potassic acetate, whilst methylic alcohol is produced and distils over; after this it may be in great measure deprived of water by the addition of potassic carbonate, and the upper stratum of liquid being decanted from the saturated aqueous solution of potassic carbonate, may be saturated with calcic chloride, which forms with methylic alcohol a compound not decomposable at the temperature of boiling water. The mixture is then subjected in a retort to the heat of a steam-bath, and the volatile portions containing acetone and methylic acetal, are thus expelled. The residue, which retains the methylic alcohol, is mixed with an equal weight of water, by which the alcohol is displaced from its combination with the chloride; and on renewing the application of heat, methylic alcohol, mixed with a little water, passes over; a second rectification from quicklime furnishes it in a state of comparative purity, and by repeating the treatment with calcic chloride the alcohol may be still further purified. Although this method, however, affords a means of obtaining pure methylic alcohol in quantity, its preparation is a matter of considerable difficulty. Crude methylic alcohol may also be purified by converting it into methylic oxalate, or still better as recommended by Carius (*Ann. Chem. Pharm.*, cx. 210) by converting it into methylic benzoate. A solution of benzoic acid in an excess of the alcohol is saturated with hydrochloric acid gas, then digested on the water bath for two or three hours, distilled, and the portion which boils above 100° (212° F.) after washing with cold water is decomposed by heating in a flask attached to a reversed condenser with a slight excess of sodic hydrate dissolved in 3 or 4 parts of water. The alcohol is distilled off, and rendered anhydrous by digesting it with quicklime. The sodic benzoate is treated with the necessary quantity of dilute sulphuric acid, and the liberated benzoic acid again employed in the preparation of a further quantity of methylic benzoate.

Properties.—Methylic alcohol is a limpid, inflammable, colourless liquid, of a penetrating spirituous odour, and a disagreeable burning taste: the empyreumatic smell commonly observed is, however, due to the impurities in the product, most of which may be removed by prolonged digestion upon charcoal and methodical filtration through it, as practised by Mr. Eschwege. It boils* at 58°·6 (137°·4 F.), and has a sp. gr. of 0·798 at 20° (68° F.), or 0·8142 at 0° (32° F.). It is soluble in water, alcohol, and ether, in all proportions. When it is mixed with water, contraction takes place. It is very inflammable, and burns with a pale non-luminous flame, producing carbonic anhydride and water, whilst its vapour passed through a red hot tube gives rise to acetylene amongst other products (Berthelot). When pure, it does not reduce mercurous nitrate if mixed with its solution. Methylic alcohol mixes readily with the essential oils, and dissolves many fatty bodies and resins with facility. Its principal application in the arts, as crude wood naphtha, is founded upon its power of dissolving the resins, which, when thus dissolved, are employed as varnishes. It is largely used for mixing with ordinary alcohol to form 'methylated spirit;' a solution of shell-lac and other resins in this, is extensively used for stiffening the basis of silk hats. The hydrates of the alkalies are soluble in wood spirit, but they immediately colour it brown, doubtless by their action on some of the impurities ordinarily present. Ure proposed to utilize this reaction as a means of detecting small quantities of pyroxylic spirit in ordinary ethylic alcohol.

When methylic alcohol, in vapour, is passed over heated soda-lime, hydrogen is given off and sodic formate is produced:

$$\underset{\text{Methylic alcohol.}}{CH_3(OH)} + NaHO = \underset{\text{Sodic formate.}}{H.COONa} + 2H_2.$$

But at higher temperatures, and in presence of excess of the alkaline hydrate, the formate is converted into oxalate, and ultimately into carbonate. Methylic alcohol also yields formic acid when slowly oxidized in contact with platinum black; the formation of the acid being probably preceded by that of formic aldehyde. The alkali metals, potassium and sodium, act with great energy on methylic alcohol, displacing the hydrogen in the OH group, and giving rise to potassic methylate, $CH_3.OK$, and sodic methylate, $CH_3.ONa$, respectively, both of which are crystalline compounds closely resembling the corresponding derivatives obtained from ethylic alcohol. With concentrated sulphuric acid, it yields hydric methylic sulphate, $CH_3.HSO_4$. Chlorine acts with great energy on the alcohol, the ultimate product, according to Cloez (*Compt. Rend.*, xlviii. 642), being *parachloralide*, C_2HCl_3O. A similar compound, *parabromalide*, C_2HBr_3O, is obtained by the action of bromine. It is not known at present, however, what is the nature of these compounds; in fact, the action of the halogens on methylic alcohol is a subject requiring investigation. Methylic alcohol dissolves calcic chloride, uniting with it to form the compound $CaCl_2 + 4CH_4O$, which crystallizes in six-sided plates. It also forms a crystalline compound with baryta, $BaO + 2CH_4O$.

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* Owing to the difficulty of obtaining it pure the boiling point of methylic alcohol is very variously stated; the number here given is that observed by Dupré (*R Soc. Proc.*, xx. 336), which there is every reason to believe is correct.

(1427) ETHYLIC ALCOHOL OR METHYLCARBINOL; *Alcohol* or *Spirit of Wine*: C_2H_6O or $CH_3.CH_2(OH)=46$.—Although intoxicating drinks prepared by the fermentation of various liquids containing sugar, such as grape juice, have been known from the earliest times, it does not appear that alcohol was obtained free from non-volatile impurities until about the twelfth century. It has been formed synthetically from ethane, acetic aldehyde, a mixture of acetic acid and acetic chloride, acetic anhydride, and also from ethylene (p. 188), by the methods described when treating of the general properties of the alcohols. The formation of alcohol from ethylene, first observed by Hennel (*Phil. Trans.*, 1826, p. 240), is of special interest as an example of the complete synthesis of a carbon compound from its elements. Thus, carbon and hydrogen, as already mentioned (p. 209), may be caused to unite directly to form acetylene, which in contact with nascent hydrogen is readily converted into ethylene. This compound is slowly absorbed when briskly agitated with concentrated sulphuric acid, and the solution when diluted with water and submitted to distillation yields a small quantity of dilute alcohol (Berthelot, *Ann. Chim.* [3], xliii. 388). According to Hemilian (*Deut. Chem. Ges. Ber.*, viii. 661) ethylic alcohol also occurs along with methylic alcohol in the product obtained by the destructive distillation of wood. This statement requires confirmation, however, as it is possible that the wood spirit referred to may have been adulterated with alcohol (*ibid.* ii. 105).

The methods just mentioned, however, possess merely a scientific interest, as alcohol is invariably prepared on the large scale by the fermentation of a saccharine solution, such as grape juice, the molasses from the sugar cane, the refuse of the beetroot sugar manufactory, starch and dextrin altered by contact with infusion of malt, &c. These solutions should contain about one-eighth of their weight of sugar, in order that the fermentation may be conducted with the greatest advantage, but even then not more than four-fifths of the whole is converted into alcohol. The reaction which produces the alcohol may be thus represented:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_6O} + 2CO_2.$$

but it must be remembered that several other products are always produced in small quantities at the same time (see Fermentation).

Alcohol may readily be obtained diluted with more or less water by subjecting these fermented *worts* to distillation. The first portions which come over contain the alcohol, and may be concentrated by repeated rectifications until they contain only about 9–10 per cent. of water. Strong spirit may, however, be obtained from the wash at a single operation by the use of specially constructed stills, similar to those devised by Adams and by Coffey (188). It is not possible, however, to separate the last portions of water by simple rectification, so that recourse must be had to some dehydrating substance. Dry potassic carbonate readily removes water from dilute alcohol, forming an aqueous solution heavier than the alcohol, and not miscible with it; and thus offers a ready method of concentrating small quantities, although it will not take up the last 4 or 5 per cent. of water. When anhydrous or "*absolute*" alcohol is required, recourse must be had to quicklime, and then the best method of proceeding is probably that given by Erlenmeyer (*Ann. Chem. Pharm.*, clx. 249). The lime is placed in small lumps in a flask or tin can furnished with an inverted condenser, highly rectified spirit is poured on to it, and the whole digested in a water bath for an hour or more. The spirit is then distilled off, and if not quite anhydrous, subjected a second time to similar treatment. Anhydrous cupric sulphate or potassic ferrocyanide may also be employed in dehydrating small quantities of alcohol. Dry alcohol does not communicate the faintest blue tinge to anhydrous cupric sulphate.

Properties.—Alcohol is a colourless, volatile, inflammable liquid, of agreeable well-known spirituous odour and burning taste. It boils at 78°·3 (173° F.), and when pure it has a specific gravity of 0·7938 at 15°·6 (60° F.) It has never been frozen, though at a temperature of – 110° C. (– 166° F.) it becomes viscid. Taken in small quantities in a diluted form, it furnishes a useful and well-known stimulant, and it forms the basis of all fermented liquors; but in large quantities it produces intoxication, and acts as a powerful narcotic poison, frequently occasioning fatal results when taken in a concentrated state, and in excess.

Alcohol, when burned in the air, emits but little light, and is wholly converted into carbonic anhydride and water, depositing no soot upon cold bodies which are introduced into its flame. Two volumes, or one molecular weight, of alcohol vapour, require for complete combustion three times its bulk, or six volumes, of oxygen; $C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$. When the vapour of alcohol is passed through a red-hot tube it is decomposed, the products varying with the temperature employed: at low temperatures, water, carbonic oxide, methane, ethylene, and acetylene appear (Berthelot); at a bright red heat carbon is deposited, and free hydrogen produced.

When alcohol is exposed to the atmosphere, it attracts moisture from it, and when mixed with water it contracts in bulk, whilst heat is at the same time developed: the observed density of the mixture of alcohol and water being greater than its calculated mean density. According to Rudberg, the condensation is greatest when 53·739 measures of alcohol and 49·836 of water are mixed at 15° (59° F.): these proportions correspond to $C_2H_6O + 3OH_2$; when cooled again to 15°, this mixture occupies only 100 measures instead of 103·575, and has a sp. gr. of 0·927 (see also Dupré and Page, *Trans. R. Soc.*, 1861, 591). From the importance of alcohol as an exciseable article, great labour has been bestowed upon the means for readily determining its percentage in spirituous liquors. The method in common use for distilled spirits consists in determining the specific gravity by means of a sensitive hydrometer; and tables have been constructed for showing the percentage of alcohol in mixtures of various densities. In these cases, great attention must be paid to the temperature, since slight differences in this particular make a material variation in the density. The term *proof spirit,* in constant use amongst the excise, is defined by an Act of Parliament (58 George III.), to be "such as shall at the temperature of 51° F. (10°·5 C.) weigh exactly twelve-thirteenth parts of an equal measure of distilled water." It consists of water 50·76, alcohol 49·24 by weight, and indicates alcohol of sp. gr. 0·920 at 15°·6 (60° F.), (0·91984; Drinkwater). The term derives its origin from the rude method of proof formerly in use, in which gunpowder was moistened with the spirit of wine to be tried, and the alcohol ignited; if it fired the powder it was said to be *over proof*, but if the spirit burnt off and left the powder damp, it was considered to be *under proof;* the weakest spirit capable of thus firing powder had a sp. gr. of about 0·920.* Every additional 0·5 per cent. of absolute alcohol above 0·920 is said to be one degree over proof.

Alcohol is a solvent of great value to the chemist, as, owing to its volatility it is easily expelled by a gentle heat, leaving the substances which it previously held in solution in a pure state. In some cases, however, it exerts a chemical action upon the bodies which it dissolves. Many of the gases are freely soluble in alcohol; some of them, as, for instance, nitrous oxide, carbonic anhydride, phosphuretted hydrogen and cyanogen, and the hydrocarbons, are dissolved by it more readily than by water. Iodine and bromine are also readily soluble in it, but their solutions gradually undergo decomposition, in consequence of the action of iodine and bromine on the alcohol. Absolute alcohol dissolves small quantities of phosphorus and of sulphur. The alkaline sulphides, as well as potassic and sodic hydrates, are soluble in it to a very large extent; and ammoniacal gas is absorbed by it nearly as readily as by water; it does not dissolve the carbonates of the alkalies, however. Alcohol likewise freely dissolves many organic bodies, such as the resins, the essential oils, the vegetable alkaloids, and many of the vegetable acids. It also dissolves, more sparingly, sugar, and the potash, soda, and ammonia soaps; but the fats and fixed oils, with the exception of castor oil, are dissolved by it only in small quantities. Alcoholic solutions of potassic and sodic hydrate, which, if concentrated, chiefly contain potassic and sodic ethylate, act powerfully as reducing agents upon many metallic solutions, such as those of platinum; they gradually absorb oxygen from the air, and become brown, owing to the formation of a resinoïd substance. When dropped upon fused potassic hydrate, alcohol is decomposed, hydrogen being evolved, and potassic acetate produced :

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* In the Appendix two tables of the strength of alcohol at different specific gravities will be found.

$$\underset{\text{Alcohol.}}{CH_3.CH_2(OH)} + KHO = \underset{\text{Potassic acetate.}}{CH_3.COOK} + 2H_2.$$

Sodium and potassium dissolve readily in alcohol with evolution of hydrogen and considerable rise of temperature, forming sodic or potassic ethylate, but these substances separate from the solution in colourless crystals in combination with alcohol, the sodium compound as $C_2H_5ONa + 3C_2H_6O$.

Chlorine attacks anhydrous alcohol with great energy, *chloral alcoholate* being the ultimate product, whilst large quantities of ethylic chloride are simultaneously produced.

The formation of chloral alcoholate is undoubtedly the end result of a long series of changes, the first of which it may be supposed takes place in accordance with the equation :

$$CH_3.CH_2(OH) + Cl_2 = CH_3.CHCl(OH) + HCl.$$

The product of this reaction probably then enters into reaction with alcohol in the following manner :

$$CH_3.CHCl(OH) + C_2H_5.OH = CH_3.CH\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right. + HCl;$$

and by the prolonged action of chlorine on this compound, chloral alcoholate is finally produced :

$$CH_3.CH\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right. + 3Cl_2 = CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right. + 3HCl.$$

The hydrochloric acid generated in these reactions converts a portion of the alcohol into monochlorethane or ethylic chloride, $C_2H_5.OH + HCl = C_2H_5Cl + OH_2$, and by the action of chlorine on this body, higher chlorinated derivatives of ethane are formed and occur in the product.

Although chloral alcoholate is the chief product of the action of chlorine on anhydrous alcohol, apparently chlorinated acetals are formed and probably also chlorinated derivatives of ethylic ether, and perhaps also chloral (Lieben, *Deut. Chem. Ges. Ber.*, iii. 907).

By the action of chlorine on aqueous alcohol, similar products are obtained, but in addition, in the early stages of the action, aldehyde, acetic acid, ethylic acetate and acetal are formed. The aldehyde is probably produced from the compound $CH_3.CHCl(OH)$, which loses a molecule of hydrochloric acid; and the acetal is perhaps formed in the manner indicated by the equation :

$$CH_3.CHCl(OH) + 2C_2H_5.OH = CH_3.CH(OC_2H_5)_2 + HCl + OH_2.$$

Bromine acts in a similar manner, but less violently (see Bromal). The action of iodine on pure alcohol is very slow, but ethylic iodide seems to be produced ultimately ; in the presence of an alkali, however, iodoform is rapidly formed, and Lieben has utilized this reaction as an extremely delicate test for alcohol. The liquid under examination is heated in a test tube, and a little iodine and potassic hydrate solution is then introduced: if alcohol is present a yellow crystalline precipitate consisting of minute hexagonal plates or six-rayed stars of iodoform soon makes its appearance. This test is capable of detecting 1 part of alcohol mixed with 10,000 of water (Hager, *Zeits. anal. Chem.*, ix. 492). Alcohol, when slowly oxidized in contact with the air, by means of platinum black for instance, yields aldehyde, $CH_3.COH$, acetal, $CH_3.CH(OC_2H_5)_2$, acetic acid, and ethylic acetate. This action may be readily observed by placing a coil of platinum wire round the wick of a spirit lamp and igniting the lamp; as soon as the portion of the coil above the wick is red-hot the flame is blown out, when the wire will continue to glow from the heat developed by the slow combustion of the alcohol, producing aldehyde, &c. Alcohol is oxidized to aldehyde by chromic acid mixture, but if an excess of the reagent be employed it is completely converted into acetic acid. When alcohol is slowly added to a well cooled mixture of concentrated nitric and sulphuric acids, ethylic nitrate, $C_2H_5.NO_3$, is produced, and this compound is also obtained when alcohol is distilled with concentrated nitric acid and urea; but concentrated nitric acid alone acts very violently on alcohol, and chiefly oxidation products, such as aldehyde, and formic, acetic, glycollic, glyoxylic and oxalic acids, and glyoxal, are formed, together with a small quantity of ethylic nitrate and ethylic nitrite (see Glyoxylic Acid). Concentrated sulphuric acid reacts with alcohol, forming hydric ethylic sulphate: $C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + OH_2$. Similarly, by the action of phosphoric acid on alcohol ethylic dihydric phosphate, $C_2H_5.H_2PO_4$, is produced; and by the action of phosphoric anhydride a mixture of diethylic hydric phosphate and triethylic phosphate is formed. The haloid acids are readily absorbed by alcohol, and when the solution is heated, monohaloid derivatives of ethane are obtained:

$$\underset{\text{Ethylic hydrate.}}{C_2H_5.OH} + HCl = \underset{\text{Chlorethane.}}{C_2H_5Cl} + OH_2.$$

When anhydrous alcohol is added to phosphorous chloride the following reactions are observed according to the proportions in which they are mixed (Wichelhaus, *Ann. Chem. Pharm. Sup.*, vi. 257):

$$PCl_3 + C_2H_5.OH = PCl_2.OC_2H_5 + HCl.$$

$$PCl_2.OC_2H_5 + C_2H_5.OH = PCl(OC_2H_5)_2 + HCl.$$

$$PCl(OC_2H_5)_2 + C_2H_5.OH = P(OC_2H_5)_3 + HCl.$$

If the alcohol contains water, secondary products are formed by its action on the chlorides; for example:

$$PCl_2.OC_2H_5 + 2OH_2 = PO_2H_2.OC_2H_5 + 2HCl.$$

Similar reactions occur with phosphoric oxychloride, $POCl_3$. By the action of phosphoric pentachloride on alcohol, phosphoric oxychloride, chlorethane, and hydrochloric acid are produced, the reaction being precisely similar to that which occurs when water decomposes the chloride:

$$PCl_5 + C_2H_5.OH = POCl_3 + C_2H_5Cl + HCl.$$
$$PCl_5 + OH_2 = POCl_3 + HCl + HCl.$$

The bromides and iodides of phosphorus behave similarly.

When anhydrous alcohol is added to well cooled thiosulphurous chloride, S_2Cl_2, it is at once acted upon, hydrochloric acid and sulphurous anhydride gases being evolved, whilst the residue contains chlorethane, ethylic sulphite, traces of mercaptan and sulphur (Carius, *Ann. Chem. Pharm.*, cvi. 291). The manner in which these various products are formed is not thoroughly understood, but probably the following equations represent the reactions which occur:

$$\alpha.\ \underset{\text{Alcohol.}}{C_2H_5.OH} + \underset{\text{Thiosulphurous chloride.}}{S_2Cl_2} = \underset{\text{Mercaptan.}}{C_2H_5.SH} + \underset{\text{Sulphurous chloride.}}{SOCl_2};$$

$$\beta.\ 2C_2H_5.SH + SOCl_2 = SO(SC_2H_5)_2 + 2HCl;$$
$$\gamma.\ SO(SC_2H_5)_2 + SOCl_2 = SO_2 + 3S + 2C_2H_5Cl.$$

By the action of chlorhydric sulphate on alcohol, diethylic sulphate is produced (Magurowska, *Journ. Pr. Chem.* [2], xiii. 158):

$$2C_2H_5.OH + SO_3Cl.OH = SO_2(OC_2H_5)_2 + OH_2 + HCl.$$

Alcoholates.—Alcohol not only dissolves many of the deliquescent salts, but also combines with various saline bodies in definite proportions, forming crystallizable compounds, in which, as Graham pointed out, the alcohol acts in the same way as water of crystallization. The calcic chloride compound, for instance, has the formula $CaCl_2 + 4C_2H_6O$; the zincic chloride compound the formula $ZnCl_2 + 2C_2H_6O$, whilst the baryta compound is $BaO + 2C_2H_6O$. Magnesic and calcic nitrates, ferrous and ferric chlorides, manganous and stannic chlorides also form crystallizable compounds with alcohol.

By cooling mixtures of alcohol and water containing not less than about 40 per cent. of alcohol in a bath of solid carbonic anhydride and ether a crystalline hydrate of alcohol, $C_2H_6O+4OH_2$, is obtained; this substance melts constantly at $-34°$ ($-29°{\cdot}2$ F.) (Guthrie, *Phys. Soc. Proc.*, 1875, p. 94).

Methylated Spirit.—The methylated spirit of commerce consists of a mixture of alcohol of sp. gr. 0·830 with 10 per cent. of common wood spirit. This addition of wood spirit scarcely interferes with the employment of the spirit as a solvent, although it renders it too unpalatable to be used as a stimulant; it was added to facilitate the use of spirit in the arts without inflicting injury on the revenue; amongst other advantages, the aid it has afforded in facilitating researches in organic chemistry in this country is very considerable. The offensive odour may be removed by prolonged contact with charcoal, as has been shown by Mr. Eschwege, but this is not permitted by the excise.

Wines, Fermented Liquors, and Spirits.—The various kinds of spirits in use derive their names from accidental circumstances—often from the flavour which they possess. For instance, *gin* is spirit flavoured by distilling it with juniper berries; *peppermint* owes its aroma to the essential oil of the plant after which it is named; *whisky* is spirit distilled from wort prepared from malt which has been dried over a peat fire, to which its peculiar flavour is due; *arrack* is a spirit distilled from fermented rice; and *rum*, a West Indian product, from molasses; *brandy* is really the 'spirit of wine,' being obtained from wines by distillation, and coloured more or less deeply with burnt sugar. In all these cases the characteristic flavour depends upon a small quantity of some volatile oil or compound ether, which passes over with the spirit during the process of distillation.

The varieties of spirits are very numerous, and those of fermented liquors which are used without subjecting them to distillation, are still greater. To this class belong all the different kinds of wine, which owe their peculiarities of flavour partly to the different varieties of grape, of which 500 or 600 are cultivated, and partly to the different flavour which even the same variety of grape* possesses when grown in different climates, or even on a different soil. The grapes grown in the hottest climates furnish the sweetest juice, but not necessarily the wines of finest quality; and the flavour is also materially influenced by the manner in which the wine is prepared. For example, when fermentation is allowed to proceed until almost all the sugar is transformed into spirit, a dry wine is produced; when checked before this point is reached, the result is a rich fruity wine; and when bottled whilst the fermentation is still proceeding, a brisk effervescent wine like champagne is the result. It is the usual practice to add more or less of a solution of pure beet or cane sugar to champagne before it is finally ready for the market. According to the experiments of Bence Jones, claret, Burgundy, and the wines of the Rhine and the Moselle, contain scarcely any sugar; sherry yields from 1 to 5 per cent., port from 3 to 7 per cent., and Tokay as much as 17 per cent. of sugar. The change of flavour consequent on the ageing of wine, depends partly upon the gradual fermentation of sugar still retained in rich wines, and partly upon the slow separation of saline matter, principally in the form of hydric potassic tartrate, $KHC_4H_4O_6$, which becomes less soluble as the proportion of spirit increases, and is deposited, particularly from port wines, as a crust of tartar upon the sides of the bottle. An important part of the change of flavour appears also to be owing to the slow formation of minute quantities of fragrant and aromatic ethers, which are gradually produced by the action of the acids present on the alcohols in the wine.

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* A certain variety of grape when grown upon the Rhine furnishes a species of Hock; the same grape when raised in the valley of the Tagus yields Bucellas; whilst in the island of Madeira it produces the wine known as Sercial, which has a flavour quite different from either of the others.

Some wines, instead of improving, become ropy by keeping. This occurs only with sweet wines, and is due to a peculiar species of fermentation in which the sugar passes into the uncrystallizable form of mucilage.

The colour of the wine is dependent upon the mode in which the fermentation is effected. Red grapes may be made to yield a 'white' wine if the husks of the grape be removed from the must before the fermentation begins, as in the preparation of champagne and sherry; but if the skins be left in the fermenting mass, the alcohol, as it is formed, dissolves the colouring matter, producing the different shades of 'red' wine. During the preparation of red wines, the skins and stalks rise to the surface of the fermenting mass and form the *chapeau*, which is removed from the fermenting juice at an earlier stage in the making of clarets than in the preparation of ports, and this is one reason why port is the more astringent wine of the two.

The process of fermentation in making wine is much more gradual and protracted than in the preparation of malt liquors. After the grapes have been trodden in the press, the juice passes to the fermenting vessels: no addition of yeast is necessary, as after a short time a copious deposit of ferment granules or yeast occurs spontaneously. The fermenting vats are so constructed that when the active stage of the fermentation is over, they can be loosely closed by a bung. As soon as the winter frost sets in, the wine is decanted from the lees into casks, which are completely filled, and then closed with care. In order to supply the loss from leakage or evaporation, the casks are carefully filled up at intervals. Here a secondary very gradual fermentation occurs, which requires careful watching; exclusion of the air at this stage being indispensable in order to prevent the wine from becoming sour, from the formation of acetic acid by the oxidation of the alcohol.

Sometimes a wine acquires a peculiar flavour known as the 'taste of the cask.' This is attributed to the development of a peculiar essential oil during the growth of fungi, or 'mould,' upon the surface of the wine (?). It is said that it may be removed by adding to each pipe about a quart of olive oil, which dissolves the obnoxious flavouring matter, and carries it with it to the surface.

It is obvious that in wines and other fermented liquors which have not been submitted to distillation, all the soluble matter of the fruit is present in the beverage. Other saccharine juices besides that of the grape, admit of being fermented, and thus a great variety of drinks may be produced. Beer and ale, for example, consist of an infusion of malt, flavoured by the aromatic bitter of the hop, and subsequently fermented. The different kinds of porter and stout are prepared in much the same way, and owe their dark colour and peculiar flavour to the use of high-dried malt; *cider* is the fermented juice of the apple: *perry* is a similar liquid obtained from the pear; and nearly every fruit may be made to yield similar beverages. Even savage nations evince a knowledge of this fact. The natives of the islands in the Pacific, when discovered by Cook, not only knew how to prepare an intoxicating liquor from the juice of the cocoa-nut, but they were accustomed to rectify it by a rude process of distillation.

Since foreign matters are present in all fermented liquors, the specific gravity would, except in special cases,* be no guide to the quantity of spirit contained in them. A simple means of overcoming this difficulty was successfully practised by Brande:—Potassic carbonate is soluble in water, but insoluble in alcohol: so that when dry potassic carbonate in powder is added to a mixture of alcohol and water until it ceases to be dissolved on agitation, the water becomes saturated with the salt, and the liquid separates into two layers, the upper of which consists of alcohol of sp. gr. 0·825. By employing a graduated tube for the experiment, the volume of alcohol which is contained in a known bulk of any wine or liquor may be read off at once by inspection.

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* See "Report on Original Gravities" by Graham, Hofmann, and Redwood (*Journ. Chem. Soc.*, v. 229).

Christison submitted different wines to distillation, in order to determine their percentage of alcohol; he thus obtained a series of results, the most important of which are embodied in the following Table. The numbers represent the weight of absolute alcohol contained in 100 parts of each variety of wine or fermented liquor.*

Port . .	from 14·97 to 17·10	Amontillado .	12·63
Dry Lisbon	16·14	Claret . . .	from 7·72 to 8·99
Madeira .	from 14·09 to 16·90	Hambacher .	7·35
Sherry . .	„ 13·98 „ 16·17	Rudesheimer .	from 6·90 to 8·40
Teneriffe .	13·64	Edinburgh ale	„ 5·70 „ 6·06
Shiraz . .	12·95	Best London porter .	5·36
Malmsey .	12·86		

(1428) PROPYLIC OR TRITYLIC ALCOHOLS: $C_3H_7.OH = 60$.—The only two isomeric alcohols of the composition $C_3H_7.OH$ which according to our present theory can exist have been obtained, viz.:

		B.P. °C.
Primary propylic alcohol or ethylcarbinol . .	$CH_3.CH_2.CH_2.OH$	97°·4
Secondary „ „ dimethylcarbinol	$CH(CH_3)_2.OH$	82°·8

The former is ordinarily termed propylic, and the latter isopropylic alcohol. They may also be distinguished as α- and β-propylic alcohols, and their derivatives as α- and β-propyl derivatives. No compounds capable of yielding propylic alcohol are produced naturally, although propyl derivatives, such as cymene or propylmethylbenzene, $C_3H_7.C_6H_4.CH_3$, and thymol or propylmethylphenol, $C_3H_7.C_6H_3(OH).CH_3$, are met with in certain plants; neither has it been conclusively proved that isopropyl compounds occur naturally, although, as already pointed out (p. 293), it is not improbable that some few at least of the terpenes are isopropyl derivatives.

(1429) *Primary Propylic Alcohol* or *Ethylcarbinol*: $C_2H_5.CH_2(OH)$.—This alcohol may be prepared in a variety of ways: from propane, propionic aldehyde, propionic anhydride, and propylamine, by the general methods already described, but it is most conveniently obtained from the crude spirit resulting from the fermentation of saccharine solutions, by the fractional distillation of that portion which remains after separating the greater part of the ethylic alcohol. It is especially abundant in the spirit obtained by fermenting cider (Pierre and Puchot, *Ann. Chem. Pharm.*, clxiii. 253).

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* Full information on the subject of wines may be derived from Dupré and Thudicum's work on wines.

The complete separation of the alcohol from its homologues by fractional distillation is extremely difficult however, if not impossible; so that, to obtain the pure alcohol, it is necessary to convert the fraction obtained by rectification into a derivative of high boiling point, such as propylic benzoate, by transforming it first into iodopropane or propylic iodide by the aid of hydriodic acid, and then into the benzoate by reacting with this compound upon argentic benzoate. After purification by fractional distillation, the propylic benzoate is saponified with potassic hydrate, the alcohol dried over ignited potassic carbonate, and rectified; it is then finally distilled from anhydrous baryta.

(1430) Propylic alcohol, according to Linnemann (*ibid.*, clxi. 26), is a colourless highly refractive liquid, possessing a strong alcoholic odour, of the specific gravity ·8066 at 15° (59° F.); it boils at 97°·4 (207°·3 F.). It burns with a smokeless but highly luminous flame; it is soluble in all proportions in water, but may be separated by the addition of easily soluble salts, such as calcic chloride or potassic carbonate; it appears to form a hydrate, $C_3H_8O+OH_2$, which boils constantly at about 87° (188°·6 F.) under the ordinary pressure. Propylic alcohol exhibits all the properties characteristic of ethylic alcohol; when oxidized it is converted first into propionic aldehyde:

$$\underset{\text{Propylic alcohol.}}{CH_3.CH_2.CH_2(OH)} + (O + OH_2) = \underset{\text{Propionic aldehyde.}}{CH_3.CH_2.COH} + 2OH_2;$$

and subsequently, on further oxidation, into propionic acid, $C_2H_5.COOH$.

Secondary Propylic Alcohol or *Dimethylcarbinol*: $CH(CH_3)_2.OH$. —This alcohol has been obtained by the application of the various general methods from propane, dimethylketone or acetone, isopropylic iodide, propylene, and isopropylamine; it is most readily prepared from isopropylic iodide (from glycerin, q.v.) by digesting it with water and plumbic hydrate (p. 413).

Like ethylic alcohol, isopropylic alcohol combines with calcic chloride, and by the aid of this compound may be purified from such substances as acetone. For this purpose, the impure anhydrous alcohol is mixed with finely-powdered anhydrous calcic chloride, so as to form a thick paste: combination occurs with development of heat, and the mass becomes solid; it is then rapidly pulverized, and exposed over sulphuric acid in vacuo, until only a dry powder remains, from which the alcohol is separated by the addition of water and distillation, &c.

Isopropylic alcohol has a great attraction for water, and appears to form several hydrates, one of which, $2C_3H_8O + OH_2$, has the same percentage composition and about the same boiling point as ethylic alcohol: the water cannot be separated from this hydrate by anhydrous cupric sulphate, and in order to dry the alcohol it must be digested with anhydrous potassic carbonate, and afterwards with ignited baryta in closed vessels, at the temperature of boiling water (Erlenmeyer, *ibid.* cxxvi. 308; Linnemann, *ibid.* cxxxvi. 38; clxi. 49).

Isopropylic alcohol is a colourless mobile liquid, possessing a faint alcoholic odour, soluble in all proportions in water; it boils at 82°·8 (181°·2 F.), and at 16° (60°·8 F.) has the specific gravity ·787. On oxidation it is converted into acetone:

$$\underset{\text{Isopropylic alcohol.}}{CH_3.CH(OH).CH_3} + (O + OH_2) = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + 2OH_2;$$

which, on further oxidation, yields acetic and formic acids. On treatment with bromine, isopropylic alcohol furnishes isopropylic bromide and brominated derivatives of acetone (Friedel); the first action is probably similar to that of bromine on ethylic alcohol, and consists in the formation of the brominated alcohol:

$$CH_3.CH(OH).CH_3 + Br_2 = CH_3.CBr(OH).CH_3 + HBr,$$

which at once splits up into acetone and hydrobromic acid; the former is converted into brominated derivatives, and by the action of the latter on unattacked alcohol isopropylic bromide is formed. The action of the halogens on propylic alcohol has not been examined.

The propyl and isopropyl compounds differ remarkably in their properties: the latter always having lower boiling points, and being less stable than the former. The behaviour of the isomeric propylic benzoates, $C_6H_5.COOC_3H_7$, affords a striking illustration of this: propylic benzoate distilling unchanged at 225° (437° F.), whereas isopropylic benzoate is entirely resolved into propylene and benzoic acid on distillation (Linnemann). Similarly, isopropylic iodide is rapidly decomposed by zinc alone at its boiling point, whilst propylic iodide is decomposed very slowly at its higher boiling point; the former is decomposed by the copper-zinc couple at about 50° (122° F.), about one-half being split up into permanent gases (propane and propylene), and the latter at about 80° (176° F.), but little permanent gas being obtained. In the presence of water or alcohol, propylic iodide is decomposed by the copper-zinc couple much less rapidly than is isopropylic iodide, the gas evolved being pure propane in the former case, but propane mixed with propylene in the latter (Gladstone and Tribe, *Journ. Chem. Soc.*, xxvi. 961).

Propylic may be converted into isopropylic alcohol by transforming it in succession into propylic iodide and propylene, combining the latter with sulphuric acid, and distilling the resulting hydric isopropylic sulphate with water; on the other hand, we may convert isopropylic into propylic alcohol by preparing from it the iodide, submitting this to the action of nascent hydrogen, and converting the propane thus formed into alcohols by the method described on p. 408. Linnemann has stated that when a solution of propylamine nitrite is decomposed by heat, only isopropylic alcohol is obtained, but the recent experiments of Meyer and Forster (*Deut. chem. Ges. Ber.*, ix. 535) tend to show that in this reaction the direct conversion of the propyl into the isopropyl compound, which was supposed by Linnemann to take place, does not occur. Thus they find that the alcohol from isopropylamine nitrite is pure isopropylic alcohol:

$$\underset{\text{Isopropylamine nitrite.}}{CH(CH_3)_2.NH_3(NO_2)} = \underset{\text{Isopropylic alcohol.}}{CH(CH_3)_2.OH} + N_2 + OH_2;$$

but a portion of the isopropylamine escapes decomposition, and a portion of the compound furnishes propylene:

$$CH(CH_3)_2.NH_3(NO_2) = CH_3.CH{=}CH_2 + N_2 + 2OH_2,$$

so that only a small amount of alcohol is produced. The alcohol from propylamine nitrite is a mixture of the two isomeric alcohols, containing about 55–60 per cent. of isopropylic alcohol; a portion of the propylamine escapes decomposition and a considerable amount of propylene is evolved. In order to explain the formation of the iso-alcohol, Meyer and Forster suppose that part of the nitrite is normally converted into the corresponding alcohol:

$$CH_3.CH_2.CH_2.NH_3(NO_2) = CH_3.CH_2.CH_2.OH + N_2 + OH_2,$$

another portion yielding propylene:

$$CH_3.CH_2.CH_2.NH_3(NO_2) = CH_3.CH{=}CH_2 + N_2 + 2OH_2;$$

and that part of the propylene so formed combines, whilst in the nascent state, with water, producing isopropylic alcohol:*

$$CH_3.CH{=}CH_2 + OH_2 = CH_3.CH(OH).CH_3.$$

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* A similar explanation may be given of the conversion of propylene bromide into acetone, observed by Linnemann (*Ann. Chem. Pharm.*, clxi. 59), which

(1431) **BUTYLIC OR TETRYLIC ALCOHOLS**: $C_4H_9.OH = 74$.—The four possible butylic alcohols of the formula $C_4H_9.OH$ are known to us—viz.:

			B.P. ° C.
Normal primary	or α-propylcarbinol .	$CH_3.CH_2.CH_2.CH_2.OH$	117°
Isoprimary	„ β-propylcarbinol .	$CH(CH_3)_2.CH_2.OH$	108°·4
Secondary	„ ethylmethylcarbinol	$C_2H_5.CH(CH_3).OH$	99°
Tertiary	„ trimethylcarbinol .	$C(CH_3)_3.OH$	82°·5

Butyl compounds are not known to occur naturally, and with the exception of isoprimary butylic alcohol, which is produced in the fermentation of saccharine liquids, these alcohols can only be obtained by artificial methods.

(1432) *Normal Primary* or *α-Butylic Alcohol* or *α-Propylcarbinol*: $C_3H_7^{\alpha}.CH_2(OH)$ or $CH_3.CH_2.CH_2.CH_2(OH)$. — This alcohol has been prepared from butyric aldehyde, butyric chloride, and butyric anhydride by the ordinary methods (Lieben and Rossi, *ibid.*, clviii. 137; Linnemann, clxi. 178; Saytzeff, *Journ. pr. Chem.* [2], iii. 82). It is a colourless, highly refractive liquid, possessing a powerful characteristic odour, and burns with a highly luminous flame; its vapour excites coughing. It boils at 116°·9—117° (242°·4—242°·6 F.), and at 0° (32° F.) has the specific gravity ·824. It does not solidify at −22° (−7°·6 F.). It does not mix with water in all proportions, but requires twelve times its bulk at 15° (59° F.) to dissolve it. On oxidation, it is converted into butyric aldehyde, $CH_3.CH_2.CH_2.COH$, and butyric acid, $CH_3.CH_2.CH_2.COOH$.

(1433) *Isoprimary* or *β-Butylic Alcohol, Iso-* or *β-Propylcarbinol*: $C_3H_7^{\beta}.OH$ or $CH(CH_3)_2.CH_2(OH)$.—This alcohol is always prepared by fractional distillation of fusel oil, but it has been obtained from isobutyric aldehyde by the action of nascent hydrogen, and from isobutylene, $(CH_3)_2C{=}CH_2$, by combining it with hypochlorous acid and reducing the resulting compound with nascent hydrogen. It closely resembles the normal primary alcohol, but boils at 108°·4 (227°·1 F.), and at 18° (64°·4 F.) has the specific gravity ·800 (the specific gravity of the normal

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apparently is an abnormal reaction, involving intramolecular change; it may be supposed that a bromopropylene is first formed:

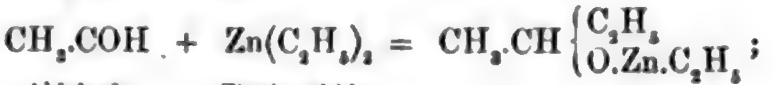
$$CH_3.CHBr.CH_2Br \;=\; CH_3.CBr{=}CH_2 \;+\; HBr,$$

and that this combines with water, the resulting compound, however, being at once split up into acetone and hydrobromic acid:

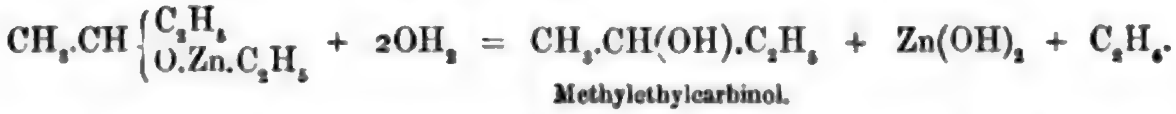
$$CH_3.CBr{=}CH_2 \;+\; HOH \;=\; CH_3.CBr(OH).CH_3,$$
$$CH_3.CBr(OH).CH_3 \;=\; CH_3.CO.CH_3 \;+\; HBr.$$

alcohol at 20° (68° F.) is ·810); it dissolves in about ten times its bulk of water at 15° (59° F.). Isobutylic alcohol, as this alcohol is ordinarily termed, furnishes isobutyric aldehyde, $CH(CH_3)_2.COH$, and isobutyric acid on oxidation.

(1434) *Secondary* or *γ-Butylic Alcohol* or *Ethylmethylcarbinol*: $C_2H_5.CH(CH_3).OH$.—This alcohol is usually prepared from secondary butylic iodide or γ-iodotetrane, $CH_3.CH_2.CHI.CH_3$, which may be produced in a variety of ways: from erythrite, from the dichlorinated ethers (p. 411, and Lieben, *Ann. Chem. Pharm.*, cl. 87), and by combining α-butylene with hydriodic acid. The alcohol has also been produced by the action of nascent hydrogen on ethylmethylketone, $C_2H_5.CO.CH_3$, and by the action of zincic methide on ethylic formate (p. 411), or of zincic ethide on ordinary aldehyde (Wagner, *Ann. Chem. Pharm.*, clxxxi. 261), the product being subsequently treated with water. This last reaction probably takes place in the manner indicated by the following equations:



$$\underset{\text{Aldehyde.}}{CH_3.COH} + \underset{\text{Zincic ethide.}}{Zn(C_2H_5)_2} = CH_3.CH\left\{\begin{matrix}C_2H_5\\ O.Zn.C_2H_5\end{matrix}\right.;$$



$$CH_3.CH\left\{\begin{matrix}C_2H_5\\ O.Zn.C_2H_5\end{matrix}\right. + 2OH_2 = \underset{\text{Methylethylcarbinol.}}{CH_3.CH(OH).C_2H_5} + Zn(OH)_2 + C_2H_6.$$

It is of especial interest as it serves to confirm the second explanation given on p. 412 of the manner in which the tertiary alcohols are formed from the acid chlorides and zinc organo-metallic compound.

Secondary butylic alcohol is a colourless liquid, possessing a pleasant alcoholic odour, and difficultly soluble in water; it boils at about 99° (210°·2 F.), and has the specific gravity ·827 at 0° (32° F.), and ·81 at 22° (71°·6 F.) (Lieben). On oxidation it furnishes ethylmethylketone:

$$C_2H_5.CH(OH).CH_3 + (O+OH_2) = C_2H_5.CO.CH_3 + 2OH_2;$$

when further oxidized this ketone yields acetic acid only.

(1435) *Tertiary* or *δ-Butylic Alcohol* or *Trimethylcarbinol*: $C(CH_3)_3.OH$.—This alcohol is prepared by the action of zincic methide on acetic chloride, and subsequent treatment of the product with water (p. 412); or by combining the so-called isobutylene, $C(CH_3)_2{=}CH_2$ with sulphuric acid, and distilling the resulting compound with water.

At ordinary temperatures trimethylcarbinol forms colourless prismatic crystals, which melt at 25° (77° F.); the liquid alcohol is an oily fluid of peculiar odour, and burns with a smoky flame. It boils at 82°·5 (180°·5 F.), and at 30° (86° F.) has the specific gravity ·7788 (Butlerow). It is soluble in all proportions in water, and forms with it a liquid hydrate, $2C_4H_8O + OH_2$, which crystallizes below 0° (32° F.) On account of the attraction which trimethylcarbinol has for water, it is extremely difficult to completely dry it, and the same remark applies to the isomeric alcohols; the last traces of water are best separated by digestion with ignited baryta. On oxidation, tertiary butylic alcohol furnishes a mixture of isobutyric and acetic acids, acetone, isobutylene and carbonic anhydride (Butlerow, *Zeits. Chem.* [2], vii. 484); probably its normal oxidation products are acetone and formic acid:

$$\underset{\text{Trimethylcarbinol.}}{C(CH_3)_3.OH} + 3(O + OH_2) = \underset{\text{Acetone.}}{CO(CH_3)_2} + \underset{\text{Formic acid.}}{H.COOH} + 4OH_2;$$

and from these compounds respectively acetic acid and carbonic anhydride are formed by further oxidation. The isobutylene may be regarded as the product of a secondary reaction, whereby the alcohol is resolved into the olefine and water:

$$C(CH_3)_3.OH = OH_2 + (CH_3)_2C{=\!=}CH_2;$$

and which is probably the result of the dehydrating action exercised by the sulphuric acid present in the oxidizing mixture. The formation of isobutyric acid may be explained by the assumption that a portion of the isobutylene thus formed combines with water producing isobutylic alcohol, which is then oxidized to isobutyric acid. The amount of isobutylene and isobutyric acid produced is relatively very small, and their formation is by no means surprising, since trimethylcarbinol is very easily resolved into the olefine and water, and isobutylene readily combines with water under the influence of acids; the only objection to this explanation is that whenever isobutylene enters into combination with other substances, such as the haloid acids and sulphuric acid, for example, it always furnishes compounds capable of yielding tertiary butylic alcohol, but it cannot be said that this must be the case under all conditions, as the circumstances under which experiments have hitherto been made are very similar.

When chlorine is passed into trimethylcarbinol, at a gentle heat, until no further action takes place, it is chiefly converted into a body having the composition of a pentachlorobutylene, $C_4H_3Cl_5$ (*Deut. chem. Ges. Ber.*, viii. 1017); it is probable, therefore, that chlorinated derivatives of the alcohol are formed which decompose into water and chlorinated derivatives of isobutylene. The action of the halogens on the isomeric alcohols has not been examined.

The stability of the isomeric butylic alcohols appears to vary directly as their boiling points, and to diminish as the boiling point diminishes; the same being true of their derivatives. Thus the elements of water are very readily abstracted from the tertiary alcohol by the action of dehydrating agents, but less readily from the secondary and isoprimary alcohols, and by no means readily from the primary alcohol. In a similar manner, olefines are formed from the haloid paraffin derivatives corresponding to these alcohols by the withdrawal of the elements of a molecule of haloid acid, and they are converted into the alcohols by treatment with moist silver oxide, or by heating with water, with increasing facility, as we pass from the primary to the isoprimary, and thence to the secondary and tertiary derivative: tertiary butylic chloride, for example, is readily converted into trimethylcarbinol by heating with water to 100° (212° F.), whilst the primary chloride is but little affected.

Many reactions are known by which the isomeric butylic alcohols may be more or less directly converted into each other. Thus the butylene obtained from the iodide formed from normal primary butylic alcohol unites with hydriodic acid to form secondary butylic iodide:

$$\underset{\text{α-Iodotetrane.}}{CH_3.CH_2.CH_2.CH_2I} - HI = \underset{\text{α-Butylene.}}{CH_3.CH_2.CH{=}CH_2};$$

$$\underset{\text{α-Butylene.}}{CH_3.CH_2.CH{=}CH_2} + HI = \underset{\text{γ-Iodotetrane.}}{CH_3.CH_2.CHI.CH_3}.$$

In the same way isobutylic alcohol may be converted into tertiary butylic iodide:

$$\underset{\text{β-Iodotetrane.}}{(CH_3)_2CH.CH_2I} - HI = \underset{\text{γ-Butylene.}}{(CH_3)_2C{=}CH_2};$$

$$\underset{\text{γ-Butylene.}}{(CH_3)_2C{=}CH_2} + HI = \underset{\text{δ-Iodotetrane.}}{CI(CH_3)_3}.$$

On the other hand, by combining the butylene from tertiary butylic alcohol with hypochlorous acid, a chlorinated alcohol convertible into isobutylic alcohol by the action of reducing agents is produced:

$$\underset{\text{δ-Iodotetrane.}}{C(CH_3)_3I} - HI = \underset{\text{γ-Butylene.}}{(CH_3)_2C{=}CH_2};$$

$$\underset{\text{γ-Butylene.}}{(CH_3)_2C{=}CH_2} + Cl.OH = \underset{\text{Chlorisobutylic alcohol.}}{(CH_3)_2CCl.CH_2.OH}.$$

In these instances the isomeric change may be traced through its various stages and readily accounted for, but this is not always the case. Thus, according to Linnemann (*Ann. Chem. Pharm.*, clxii. 3), the nitrite of normal butylamine, when decomposed by distilling its aqueous solution, does not furnish *normal* but *iso*primary butylic alcohol:

$$CH_3.CH_2.CH_2.CH_2.NH_3(NO)_2 = CH(CH_3)_2.CH_2.OH + N_2 + OH_2;$$

Normal butylamine nitrite. Isoprimary butylic alcohol.

and in a similar manner, *iso*butylamine nitrite yields *tertiary* butylic alcohol (*ibid.* 22):

$$CH(CH_3)_2.CH_2.NH_3(NO_2) = C(CH_3)_3.OH + N_2 + OH_2.$$

Isoprimary butylamine nitrite. Tertiary butylic alcohol.

Since Meyer and Forster have shown, however, that a similar statement by Linnemann with regard to the decomposition of propylamine nitrite is inaccurate, some doubt may be felt as to the extent to which these results are reliable. Supposing, however, that the reactions which take place are similar to those which Meyer and Forster regard as probable in the case of the conversion of normal propylamine into isopropylic alcohol (p. 437), the formation of the *tertiary* butylic alcohol from isoprimary butylamine does not appear improbable; but their explanation would scarcely apply to the conversion of the *normal* amine into the *isoprimary* alcohol, since the butylene from normal butyl compounds combines with other compounds to form *secondary* and not *isoprimary* derivatives. It cannot, in fact, without undergoing isomeric change, furnish *secondary* butylic compounds, as will be evident on inspection of the following formulæ:

$$CH_3.CH_2.CH_2.CH_2.X - HX = CH_3.CH_2.CH{=}CH_2;$$

Normal butyl compound. α-Butylene.

$$CH_3.CH_2.CH{=}CH_2 + HX = CH_3.CH_2.CHX.CH_3.$$

α-Butylene. Secondary compound from α-butylene.

$$(CH_3)_2CH.CH_2X.$$

Isoprimary butyl derivative.

According to Linnemann, when a mixture of isoprimary butylic iodide with glacial acetic acid is added to argentic or mercuric oxide, action takes place at ordinary temperatures, which is completed by warming on the water bath, and a mixture of tertiary butylic alcohol and tertiary butylic acetate is produced, and some isobutylene is evolved, together with a small quantity of gas not absorbed by bromine (*loc. cit.*, 14), and he recommends this process for the preparation of the alcohol; but Butlerow states (*ibid.* clxviii. 143) that the alcohol produced by this method is a mixture of about equal parts of isoprimary and tertiary butylic alcohol. The formation of the tertiary alcohol in this manner may be explained by supposing that the isoprimary iodide is converted by the action of the argentic oxide into isobutylene, which combines with the acetic acid, forming tertiary butylic acetate:

$$\underset{\gamma\text{-Butylene.}}{(CH_3)_2C{=}CH_2} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Tertiary butylic acetate.}}{(CH_3)_3C.C_2H_3O_2}.$$

Isobutylic bromide similarly treated with mercuric oxide also yields some trimethylcarbinol, but does not enter into reaction with argentic oxide; isobutylic chloride dissolved in acetic acid is scarcely acted upon by either of these oxides.

It is stated that when well cooled isobutylic iodide and iodine chloride are carefully mixed together, the former is converted into tertiary butylic chloride (Linnemann, *loc. cit.*):

$$\underset{\text{Isoprimary butylic iodide.}}{(CH_3)_2CH.CH_2I} + ICl = \underset{\text{Tertiary butylic chloride.}}{(CH_3)_3CCl} + I_2.$$

At present it appears to be impossible to give any satisfactory explanation of this remarkable reaction.

Again, Freund has shown (*Journ. pr. Chem.* [2], xii. 25), that when isoprimary butylic alcohol is mixed with a considerable excess of hydrochloric, hydrobromic, or hydriodic acid, the alcohol being also saturated with the gaseous acid, and the mixture heated for several hours in closed vessels to 100° (212° F.), the resulting chloride, bromide, or iodide is a mixture of the isoprimary with a very considerable proportion—as much as 35 per cent. in the case of the chloride—of the tertiary compound,* and since the tertiary haloid butyl compounds are readily converted into the alcohol by heating with water at 100° (212° F.), whilst the isoprimary compounds are but little acted upon, this reaction affords a ready means of preparing considerable quantities of trimethylcarbinol. It may be supposed, in explanation of the conversion, that the isobutylic alcohol, or the haloid paraffin formed from it in presence of the strong acid, is resolved into isobutylene and water or haloid acid, and that the isobutylene then combines with the haloid acid to form the tertiary derivative; it is remarkable, however, that when the alcohol is merely saturated with the gaseous acid, and the mixture heated, little, if any, of the tertiary compound is produced.

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* Freund's experiments show that the greatest caution must be exercised in judging of the constitution of compounds from the behaviour of derivatives formed from them, even by the simplest reactions. They also afford an explanation of the supposed occurrence of trimethylcarbinol in fusel oil (Butlerow, *Ann. Chem. Pharm.*, cxliv. 34), since it was *detected* and separated by converting fermentation butylic alcohol into the chloride, and heating the latter with water, &c.

Lastly, it may be pointed out that isobutylene bromide is said to be converted into isobutylic aldehyde by heating with 10—20 times its volume of water to 150°—160° (302°—320° F.) for 24 hours (Linnemann and Zotta, *loc. cit.*, p. 33), and probably also *α*-butylene bromide may in a similar manner be converted into ethylmethylketone (Linnemann, *ibid.*, p. 3). The formation of these compounds may be regarded as the final result of a series of changes similar to those which in all probability occur in the conversion of propylene bromide into acetone (p. 437), and in which, perhaps, the following compounds are successively produced:

$(CH_3)_2CBr.CH_2Br$;	$(CH_3)_2C{=\!=}CHBr$;	$(CH_3)_2CH.CHBr(OH)$;	$(CH_3)_2CH.COH$.
Isobutylene bromide.	Bromobutylene.		Isobutyric aldehyde.
$C_2H_5.CHBr.CH_2Br$;	$C_2H_5.CBr{=\!=}CH_2$;	$C_2H_5.CBr(OH).CH_3$;	$C_2H_5.CO.CH_3$.
Normal butylene bromide.	Bromobutylene.		Ethylmethylketone.

The investigation of these cases of *isomeric change* is of very great interest; and it will be obvious that whilst many of them may be explained as the result of a series of changes, others cannot, at least at present, be so explained, but must be regarded as the direct result of *intramolecular* change, in which there is no splitting off and recombination of elements, but a rearrangement of the atoms in the molecule. Many chemists are disinclined to believe in the occurrence of changes of the latter kind, so that the investigation of the nature of these reactions is of the highest importance as a step towards the explanation of isomeric change.

(1436) AMYLIC OR PENTYLIC ALCOHOLS.—Although seven of the eight possible amylic alcohols have already been obtained, most of them have been but very insufficiently investigated:

			B.P. °C.
Primary	Butylcarbinol	$CH_3.CH_2.CH_2.CH_2.CH_2.OH$	137°
	Isobutylcarbinol . . .	$CH(CH_3)_2.CH_2.CH_2.OH$	131°
	Secondary-butylcarbinol .	$C_2H_5.CH(CH_3).CH_2.OH$	128°
Secondary	Propylmethylcarbinol . .	$C_3H_7{}^{\alpha}.CH(CH_3).OH$	120°
	Diethylcarbinol	$C_2H_5.CH(C_2H_5).OH$	117°
	Isopropylmethylcarbinol .	$C_3H_7{}^{\beta}.CH(CH_3).OH$	104°
Tertiary	Ethyldimethylcarbinol . .	$C_2H_5.C(CH_3)_2.OH$	102°

These, with the exception of the two isoprimary alcohols, have only been obtained by synthetical methods (Wagner and Saytzeff, *Ann. Chem. Pharm.*, clxxv. 332).

(1437) *Normal Primary Amylic Alcohol or Butylcarbinol:* $C_4H_9{}^{\alpha}.CH_2(OH)$ or $CH_3.CH_2.CH_2.CH_2.CH_2(OH)$.—The pure alcohol has been prepared by the action of nascent hydrogen on normal valeric aldehyde (Lieben and Rossi, *Ann. Chem. Pharm.*, clix. 70); a mixture of normal primary and of secondary amylic alcohol is obtained by the conversion into alcohols of the mixture of chloropentanes formed on chlorinating normal pentane (Schorlemmer, *ibid.*, clxi. 268).

It is a colourless liquid, resembling the fermentation alcohol in odour and other properties; it boils at 137° (278°·6 F.), and at 0° (32° F.) has the specific gravity ·8296. It is converted into normal valeric acid, $C_4H_9{}^{\alpha}.COOH$ on oxidation.

(1438) *Isoprimary Amylic Alcohols. Isobutylcarbinol:* $C_4H_9{}^{\beta}.CH_2(OH)$ or $CH(CH_3)_2.CH_2.CH_2(OH)$. *Secondary-butylcarbinol:* $C_4H_9{}^{\gamma}.CH_2(OH)$ or $C_2H_5.CH(CH_3).CH_2(OH)$.—The chief constituent of *fusel oil*, or the portion of higher boiling point which remains after the separation of the greater part of the ethylic alcohol from the crude spirit produced by fermentation, is a mixture of these two alcohols. Their complete separation is very difficult, however, and cannot be effected by distillation; but they are readily distinguished, since one of them is optically inactive, whilst the other (secondary-butylcarbinol) turns the plane of polarization of a ray of light to the left, a property by which it is distinguished from all other known alcohols.

The method by which the two alcohols were originally separated by Pasteur in 1855, or rather by which the existence of two isomeric alcohols in fusel oil was first demonstrated, consists in acting upon the mixture with concentrated sulphuric acid, neutralizing with baric carbonate, and fractionally crystallizing the resulting mixture of baric amylic sulphates; the product from the active alcohol being considerably more soluble than the corresponding inactive derivative, the two salts may thus be separated, and the alcohols obtained from them by distillation with dilute sulphuric acid:

$$\underset{\text{Baric amylic sulphate.}}{(C_5H_{11}.SO_4)_2Ba} + 2OH_2 = \underset{\text{Amylic alcohol.}}{2C_5H_{11}.OH} + BaSO_4 + H_2SO_4.$$

For this purpose the portion of fusel oil is employed, which, after repeated distillation, boils at about 129° (264°·2 F.); it is mixed with about an equal weight of sulphuric acid, the latter being gradually added to the alcohol, and the mixture allowed to stand in a warm place for several days before it is added to water and the solution neutralized. When fusel oil containing a large proportion of the inactive modification is employed, it is possible to isolate it in a state of purity; but the method does not appear to be applicable to the preparation of the active modification in a state of purity, since the statements of various observers as to the rotatory power of the alcohol are most discrepant (Ley, *Deut. chem. Ges. Ber.*, vi. 1362); and even to obtain it approximately pure involves the expenditure of a large amount of material and much time and labour.

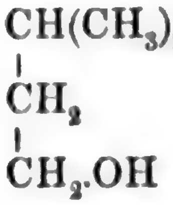
From Le Bel's experiments (*ibid.*, vi. 1314; vii. 824; ix. 732) it appears, however, that different acids behave differently with the two alcohols: the inactive alcohol having a greater tendency to enter into reaction with hydrochloric, hydriodic, and tartaric acids, whilst the active alcohol appears more readily to enter into reaction with sulphuric and valeric acids than the inactive alcohol. On this Le Bel founds a method for the preparation of the active alcohol, which consists in saturating the mixture of alcohols with hydrochloric acid gas, and then heating to 100° (212° F.), whereby the inactive alcohol is converted into amylic chloride, the active alcohol remaining for the most part unattacked; the chloride and alcohol are then separated by distillation, and the latter again similarly treated, until, in fact, the optical activity is no longer increased.

The inactive alcohol boils at about 131° (267°·8 F.), and the active at about 128° (269°·4 F.), and the latter has a slightly lower specific gravity than the former (Ley). The rotatory power of the most active alcohol yet prepared by Pasteur's method was 46°, in a column 500 mm. long, which is equal to that of a solution of cane sugar containing 4·7 grams of sugar to 100 of water (Ley). According to Le Bel, the alcohol which he separated by his method had a rotatory power of 4° 38′ in a column 100 mm. long, but as he does not state what instrument was employed, this number cannot be compared with that given by Ley, who used a Soleil-Ventzke instrument.

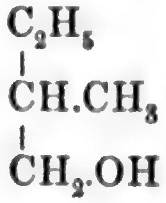
Both are colourless liquids possessing a peculiar penetrating unpleasant odour and burning taste, and are nearly insoluble in water; their vapours excite coughing. Most of the statements in the text books with regard to the reactions of amylic alcohol refer to the behaviour of the mixture of alcohols from fusel oil, which is ordinarily spoken of as amylic alcohol; in fact, scarcely any of the derivatives of these alcohols have been obtained in a state of purity.

On oxidation, both furnish in the first instance valeric aldehydes, which, on further oxidation, are converted into valeric acids, $C_4H_9.COOH$; the acid from the active alcohol is also optically active, but dextro-rotatory, and it is also distinguished by forming a gummy baric salt, the baric salt from the inactive acid being crystalline. When an 8 per cent. solution of chromic acid is employed to effect the oxidation, a considerable amount of amylic valerate is produced, but with a 5 per cent. solution (1 litre water; 105 grams H_2SO_4; and 78 grams $K_2Cr_2O_7$) this is no longer the case. The two alcohols are oxidized with very different degrees of readiness, however, the active alcohol being much more readily attacked, and even when a feebly oxidizing mixture is employed, much of the active valeric acid undergoes further oxidation to acetic acid and carbonic anhydride; both valeric acids are readily oxidized by a saturated solution of potassic dichromate in a mixture of 2 vols. water and 1 vol. sulphuric acid, being converted into acetic acid, water and carbonic anhydride; but the inactive acid yields considerably more carbonic anhydride than the active (Erlenmeyer and Hell, *Ann. Chem. Pharm.*, clx. 294; Pedler, *Journ. Chem. Soc.*, xxi. 74; Ley, *loc. cit.*).

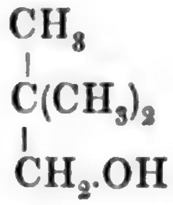
The behaviour on oxidation is of great importance, as it enables us to determine the constitution of the two alcohols from fusel oil. Since both furnish valeric acids on oxidation they must be primary alcohols, and as the normal primary amylic alcohol is not identical with either, they can only be isoprimary alcohols; but three isoprimary amylic alcohols can exist, viz.:



$$\begin{array}{l} CH(CH_3)_2 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} ;$$

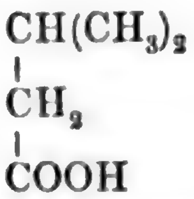


$$\begin{array}{l} C_2H_5 \\ | \\ CH.CH_3 \\ | \\ CH_2.OH \end{array} ;$$



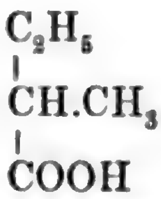
$$\begin{array}{l} CH_3 \\ | \\ C(CH_3)_2 \\ | \\ CH_2.OH \end{array}$$

These three alcohols will furnish the three following valeric acids on oxidation:



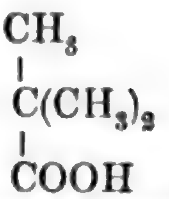
$$\begin{array}{l} CH(CH_3)_2 \\ | \\ CH_2 \\ | \\ COOH \end{array} ;$$

Isopropacetic acid.



$$\begin{array}{l} C_2H_5 \\ | \\ CH.CH_3 \\ | \\ COOH \end{array} ;$$

Methethacetic acid.



$$\begin{array}{l} CH_3 \\ | \\ C(CH_3)_2 \\ | \\ COOH \end{array}$$

Trimethacetic acid.

The first of these has been obtained by Erlenmeyer and Hell (*loc. cit.*, p. 264) from isobutylic iodide by the following reactions:

$$\underset{\text{Isobutylic iodide.}}{CH(CH_3)_2.CH_2I} + KCN = \underset{\text{Isobutylic cyanide.}}{CH(CH_3)_2.CH_2.CN} + KI;$$

$$\underset{\text{Isobutylic cyanide.}}{CH(CH_3)_2.CH_2.CN} + OH_2 + NaOH = \underset{\text{Sodic isovalerate.}}{CH(CH_3)_2.CH_2.COONa} + NH_3.$$

The acid separated from this sodic salt was found to be identical with that formed on oxidizing the inactive alcohol from fusel oil, thus proving that this alcohol is represented by the formula $CH(CH_3)_2.CH_2.CH_2(OH)$. Trimethacetic acid has also been synthetically prepared, and differs entirely in its properties from the active valeric acid from the active amylic alcohol; hence it follows that the active alcohol has the formula $C_2H_5.CH(CH_3).CH_2(OH)$, unless we assume that it is merely physically isomeric with the inactive modification, as some chemists have supposed; but this assumption is not admissible since, according to Le Bel, the iodide prepared from it furnishes an optically inactive amylene, boiling at 31°—32° (87°·8—89°·6 F.),* different from the amylene (B.P. 25° C.) from the iodide formed from the inactive alcohol:

$$\underset{\text{Iodide from active alcohol.}}{C_2H_5.CH(CH_3).CH_2I} + KHO = \underset{\beta\text{-Ethylmethylethylene.}}{C_2H_5.C(CH_3){=}CH_2} + KI + OH_2.$$

$$\underset{\text{Iodide from inactive alcohol.}}{CH(CH_3)_2.CH_2.CH_2I} + KHO = \underset{\text{Isopropylethylene.}}{CH(CH_3)_2.CH{=}CH_2} + KI + OH_2.$$

This amylene combines in the cold with hydrochloric acid, forming a chloropentane convertible into the isomeric amylene, trimethylethylene, by the action of potassic hydrate:

$$CH_3.CH_2.C(CH_3){=}CH_2 + HCl = CH_3.CH_2.CCl(CH_3).CH_3;$$
$$CH_3.CH_2.CCl(CH_3).CH_3 + KHO = CH_3.CH{=}C(CH_3).CH_3 + KCl + OH_2.$$

Moreover Saur has recently succeeded (*Deut. chem. Ges. Ber.*, viii. 1037) in preparing methethacetic acid synthetically, and finds that it resembles the active valeric acid from active amylic alcohol in its properties, and that it yields a non-crystalline baric salt; so that there can no longer be any doubt as to the constitution of active amylic alcohol.

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* This amylene has the specific gravity ·670 at 0° (32° F.); it should be inserted in the table p. 184, in the column headed Series $H_2C{=}C(C_nH_{2n+1})_2$. According to Le Bel, pure trimethylethylene boils at 36°—38° (96°·8—100°·4 F.), and at 0° (32° F.) has the specific gravity ·6783; it also combines with hydrochloric acid in the cold.

Many of the derivatives of active amylic alcohol are themselves active, but it is remarkable that they are dextrorotatory. According to Le Bel, the rotatory powers of the chloride, bromide, and iodide prepared from the alcohol form a proportional series, and are related to each other as the numbers 1, 4, and 8.

If sodic or potassic hydrate, calcic chloride, or apparently any salt easily soluble in the alcohol, be dissolved in ordinary amylic alcohol at the boiling point, and the saturated solution be distilled from an oil bath, finally at about 200° C., a considerable amount of the alcohol is retained in the retort, and when this is liberated by adding water and again distilling, it is found that the alcohol which passes over is considerably less active than that originally employed (Chapman and Smith, *Proc. R. Soc.*, xvii. 308). If sodium be dissolved in active amylic alcohol, the excess of the latter distilled off in the oil bath, the alcohol liberated from the sodium compound by the addition of water and, after drying, again similarly treated, it is rendered inactive; this change appears to be produced by the heating, and is not a specific action of the sodium (Le Bel). The alcohol is apparently not altered in its chemical properties (Le Bel); and this is the more probable since Erlenmeyer and Hell have shown that when active valeric acid is heated to 250° (482° F.) with a few drops of concentrated sulphuric acid for at most fifteen minutes, it entirely loses its optical activity, but is not altered in chemical properties.

Sodium dissolves in amylic alcohol, forming sodic amylate, which separates in crystals of the composition $C_5H_{11}.ONa + 3C_5H_{12}O$. When a solution of sodic hydrate in amylic alcohol is distilled, water passes over (Chapman):

$$\underset{\text{Amylic alcohol.}}{C_5H_{11}.OH} + NaOH = \underset{\text{Sodic amylate.}}{C_5H_{11}.ONa} + OH_2,$$

so that distillation from sodium cannot be resorted to as a method of rendering amylic alcohol anhydrous.

In all its reactions amylic alcohol (fusel oil) closely resembles ethylic alcohol, but it is a much less stable compound.

(1439) *Sec. Amy. Alcohols. Propylmethylcarbinol:* $C_3H_7{}^a.CH(CH_3).OH$. —This alcohol is formed by the action of nascent hydrogen on propylmethylketone, $C_3H_7.CO.CH_3$, and, together with normal primary amylic alcohol, from normal pentane by Schorlemmer's method. It has also been prepared from the amylic iodide obtained by combining *a*-amylene (1232) with hydriodic acid. It boils at about 120° (248° F.), and at 0° (32° F.) has the specific gravity ·826; on oxidation it yields a ketone of the formula $C_5H_{10}O$, and propionic and acetic acids (Wurtz).

Diethylcarbinol: $(C_2H_5)_2CH.OH$, is obtained by the action of zincic ethide on ethylic formate, and subsequent treatment of the product with water (Wagner and Saytzeff, *Ann. Chem. Pharm.*, clxxv. 363). It is a colourless liquid, difficultly soluble in water, possessing the peculiar odour characteristic of the amylic alcohols; it boils at 116°—117° (240°·8—242°·6 F.), and at 0° (32° F.) has the specific gravity ·832. On oxidation it furnishes diethylketone, propionic acid and acetic acid.

Isopropylmethylcarbinol: $C_3H_7\beta.CH(OH).CH_3$, is formed from the amylene from isoprimary amylic iodide[*] by combining it with hydriodic acid, digesting the resulting iodide with dry argentic acetate, and decomposing the amylic acetate with a concentrated aqueous solution of potassic hydrate (Flavitzsky, *ibid.*, clxxix. 348). It has also been obtained from methylisopropylketone by the action of nascent hydrogen (Münch, *ibid.*, clxxx. 339). The alcohol from amylene is said to boil at 103°—104° (217°·4—219°·2 F.), and on oxidation with a five per cent. solution of chromic anhydride, it furnishes acetone and acetic acid, no isopropylmethylketone being formed; its specific gravity at 0° (32° F.) is ·826. The alcohol prepared from the ketone is a liquid of pleasant ethereal odour, of the specific gravity ·827 at 17° (62°·6 F.); it is stated to boil at 108° (226°·4 F.), and to be reconverted into the ketone on oxidation.

(1440) *Tertiary Amylic Alcohol* or *Ethyldimethylcarbinol:* $C_2H_5.C(CH_3)_2.OH$, may be prepared by the action of zincic methide on propionic chloride, $C_2H_5.COCl$, the product being subsequently treated with water (Popoff, *ibid.*, cxlv. 292; Ermolaiew, *ibid.*, clxii. 190). This alcohol has a peculiar aromatic odour, different from that of its isomerides, and is also more soluble in water. It solidifies at about −30° (−22° F.) to a mass of small needles, and boils at 98°·5−102° (209°·3−215°·6 F.) (Ermolaiew).

The so-called amylene hydrate obtained by combining amylene from fermentation amylic alcohol with hydriodic acid and treating the resulting amylic iodide with moist argentic oxide (Wurtz), or by combining it with sulphuric acid and then distilling with water (Flavitzsky, p. 195; *ibid.*, clxxix. 343), appears to be this alcohol.[†] It boils at 102° (215°·6 F.), and on oxidation by a 5 per cent.

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[*] The amylic iodide employed by Flavitzsky contained a certain amount of the active iodide, and the amylene prepared from it, therefore, was a mixture of isopropylethylene, $H_2C{=}CH.C_3H_7^{\beta}$, with ethylmethylethylene, $C_2H_5.C(CH_3){=}CH_2$; hence the alcohol probably contained a certain amount of ethyldimethylcarbinol, and this may account for the low boiling point observed by Flavitzsky as compared with that observed by Münch.

[†] According to Ossipoff (*Deut. chem. Ges. Ber.*, viii. 1240), different alcohols are produced when sulphuric acid of different degrees of concentration is employed. By adding the amylene drop by drop to a well-cooled mixture of 2 pts. *by weight* of sulphuric acid and 1 pt. of water (as employed by Flavitzsky) and subsequently distilling with water, he obtained an alcohol boiling at 102°−105° C., which did not solidify when cooled to −30° C.; but with a mixture of 2 *vols.* of sulphuric acid (about 3·6 pts. by weight) and 1 vol. of water an alcohol boiling at about 97° C was produced, which readily solidified between −20° and −30° C., and which had not the same odour as the alcohol of higher boiling point. Amylene hydrate, also, which he prepared from the amylic iodide from amylene by Wurtz's method, did not solidify at −30° C. Although Ossipoff concluded from this that the two alcohols he obtained were isomeric, and respectively identical with ethyldimethylcarbinol and amylene hydrate—adopting the view then prevalent that the latter was isopropylmethylcarbinol—it appears highly probable that the two alcohols in question are really identical, and that the

solution of chromic anhydride yields acetone and acetic acid (Flavitzsky). Amylene hydrate is remarkable on account of the great readiness with which it is resolved into amylene and water,—hence its name; this decomposition takes place when its vapour is heated to 200° (392° F.), on mixing it with sulphuric acid, or when it is heated with acetic acid in the water-bath; similarly, when

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difference observed in the products was due to the presence of impurity; for we may now regard it as an established fact that amylene prepared from fermentation amylic alcohol by the action of zincic chloride is trimethylethylene (see Amylglycols). From Henry's more recent experiments it appears that the statement on p. 401 that propylene may combine with hypochlorous acid in two ways is incorrect, and that the compound $CH_3.CHCl.CH_2(OH)$ is always produced (comp. p. 462). The behaviour of hypochlorous acid with olefines, therefore, resembles that of the haloid acids, and we have consequently little reason to expect that the behaviour of sulphuric acid will prove exceptional; so that, according to the law which regulates the combination of the olefines with the haloid acids (p. 400), trimethylethylene will furnish a tertiary amylic derivative when combined with sulphuric acid:

$$(CH_3)_2C{=}CH.CH_3 + H_2SO_4 = (CH_3)_2C(HSO_4).CH_2.CH_3,$$

the alcohol from which would be ethyldimethylcarbinol. Even supposing, however, that the complementary reaction:

$$(CH_3)_2C{=}CH.CH_3 + H_2SO_4 = (CH_3)_2CH.CH(HSO_4).CH_3,$$

is possible, it is highly improbable that the one would take place *to the exclusion* of the other by a comparatively slight variation in the concentration of the acid, as was the case in Ossipoff's experiments. Therefore, admitting the action of sulphuric acid on amylene to vary with the concentration, it is improbable that in the one experiment only the tertiary alcohol and in the other only the secondary was produced, which is the interpretation Ossipoff places upon his results.

The production of trimethylethylene from fermentation amylic alcohol is doubtless the final result of a series of changes. It is not improbable that in the first instance the zincic chloride and alcohol enter into reaction to produce zincic chloramylate:

$$ZnCl_2 + C_5H_{11}OH = ZnCl.OC_5H_{11} + HCl,$$

and that this compound is subsequently resolved into amylene and ZnCl.OH, thus:

$$ZnCl.OC_5H_{11} = C_5H_{10} + ZnCl.OH.$$

These reactions, it will be observed, are the counterpart of those which occur in the formation of ethylene from sulphuric acid and ethylic alcohol. In this manner, the amylene, isopropylethylene, would be formed from the isoprimary-butylcarbinol, and the isomeric ethylmethylethylene from the secondary butylcarbinol present in the fermentation alcohol. Both these amylenes, however, combine with hydrochloric acid, and furnish the *same* amylic chloride: and the tertiary amylic chloride thus produced is readily resolved into hydrochloric acid and the amylene, trimethylethylene. The supposition, therefore, that these two inverse reactions actually occur, is perfectly warranted, and appears to afford a simple explanation of the isomeric change observed in the formation of trimethylethylene from the fermentation alcohols. The action of zincic chloride on fermentation amylic alcohol, however, is a subject requiring investigation on account of the occurrence of other hydrocarbons besides amylene and its polymerides in the product (p. 194); the formation of paraffins is not yet explained, and it has to be shown whether, as Wurtz supposes, all the products are derived from amylic alcohol, or in part from other alcohols.

mixed with bromine at ordinary temperatures, it furnishes water and an amylene bromide. Its haloid derivatives are equally unstable, the iodide being reconverted into the alcohol by mere digestion with moist argentic oxide at 0° (32° F.), whereas the iodide from fermentation amylic alcohol is scarcely acted upon below 100° (212° F.).

(1441) HEXYLIC ALCOHOLS: $C_6H_{13}.OH = 102$.—No less than eight isomeric hexylic alcohols have been described, but most of them have been comparatively little studied:

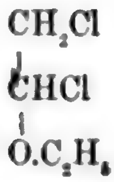
			B.P. °C.
Primary	Pentylcarbinol	$C_5H_{11}{}^{\alpha}.CH_2.OH$	157°
	Isoprimary-pentylcarbinol	$C_5H_{11}{}^{\beta}.CH_2.OH$	148°–154°
Secondary	Butylmethylcarbinol	$C_4H_9{}^{\alpha}.CH(CH_3).OH$	135°—138°
	Propylethylcarbinol	$C_3H_7{}^{\alpha}.CH(C_2H_5).OH$	135°
	Tertiary-butylmethylcarbinol	$C_4H_9{}^{\delta}.CH(CH_3).OH$	120°·5
Tertiary	Diethylmethylcarbinol	$(C_2H_5)_2C(CH_3).OH$	119°—121°
	Propyldimethylcarbinol	$(CH_3)_2C(C_3H_7)^{\alpha}.OH$	114°—117°
	Isopropyldimethylcarbinol	$(CH_3)_2C(C_3H_7)^{\beta}.OH$	112°—113°

(1442) *Primary Hexylic Alcohols. Normal Primary Hexylic Alcohol:* $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2(OH)$.—The essential oil of *Heracleum giganteum* contains a considerable amount of hexylic acetate, the portion boiling at about 201°—206° (393°·8—402°·8 F.) being a mixture of this ether and octylic butyrate; from this, hexylic and octylic alcohols may be obtained by saponification with an alcoholic solution of potassic hydrate, and then separated by fractional distillation (Franchimont and Zincke, *Ann. Chem. Pharm.*, clxiii. 193).

The hexylic alcohol thus obtained is a colourless oily liquid of pleasant aromatic odour and insoluble in water. It boils at 157° (314°·6 F.), and at 23° (73°·4 F.) has the specific gravity ·819. On oxidation, it furnishes normal caproic acid, $C_5H_{11}.COOH$.

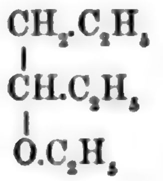
Isoprimary Hexylic Alcohol: $(CH_3)_2CH.CH_2.CH_2.CH_2(OH)$. — Faget in 1853 separated from brandy fusel oil, a portion boiling at 148°—154° (298°·4—309°·2 F.), which he states gave caproic acid on oxidation; he regarded it as caproylic or hexylic alcohol, and from the boiling point it appears not improbable that the substance he obtained was the next homologue of fermentation amylic alcohol (compare also Wurtz, *Ann. Chem. Pharm.*, cxxviii. 316). No attempt appears to have been made since then to isolate this alcohol from fusel oil, but its re-discovery and investigation are much to be desired.

(1443) *Secondary Hexylic Alcohols. Primary-butylmethylcarbinol:* $CH_3.CH_2.CH_2.CH_2.CH(CH_3).OH$.—A mixture of this alcohol with primary hexylic alcohol is obtained from normal hexane by chlorination, &c., according to Schorlemmer's method. The pure alcohol is produced by the action of moist argentic oxide on the secondary hexylic iodide from mannite, or by combining the hexylene obtained from this iodide with sulphuric acid, and distilling the product with water (Erlenmeyer and Wanklyn; Hecht, *Ann. Chem. Pharm.*, clxv. 146). By the action of zincic ethide on dichlorinated ethylic ether, Lieben (*ibid.*, clxxviii. 1) has obtained a diethylether, which, by the action of hydriodic acid, may be converted into a hexylic iodide; this, when treated with argentic acetate and glacial acetic acid, yields an acetate from which butylmethylcarbinol may be obtained on saponification. The formation of butylmethylcarbinol in this manner, however, is the result of isomeric change, and that this is the case will be evident from the following formulæ:



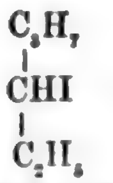
$$\begin{array}{c} CH_2Cl \\ | \\ CHCl \\ | \\ O.C_2H_5 \end{array}$$

Dichlorether.



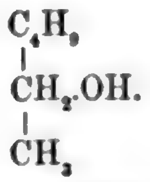
$$\begin{array}{c} CH_2.C_2H_5 \\ | \\ CH.C_2H_5 \\ | \\ O.C_2H_5 \end{array}$$

Diethylether.



$$\begin{array}{c} C_3H_7 \\ | \\ CHI \\ | \\ C_2H_5 \end{array}$$

Hexylic iodide from diethylether.



$$\begin{array}{c} C_4H_9 \\ | \\ CH_2.OH. \\ | \\ CH_3 \end{array}$$

Butylmethylcarbinol.

The change probably occurs when the iodide is submitted to the action of acetic acid and argentic acetate, the iodide being first converted into the hexylene, propylmethylethylene, $C_3H_7.HC{=}CH.CH_3$, which combines with the acetic acid, forming the acetate of butylmethylcarbinol. A similar change in the butyl series has been mentioned previously (p. 442).

Butylmethylcarbinol is a colourless liquid, insoluble in water, possessing a pleasant alcoholic but also aromatic odour; it boils at 135°—138° (275°—280°·4 F.); the specific gravity of the alcohol from hexylene is ·8266 at 0° (32° F.), according to Hecht. On careful oxidation, it is converted into butylmethylketone, which on further oxidation yields normal butyric acid, $C_3H_7.COOH$, and acetic acid.

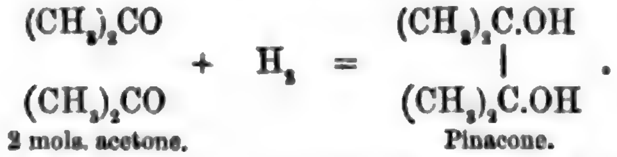
Propylethylcarbinol: $C_3H_7.CH(C_2H_5).OH$, is formed from ethylpropylketone by the action of nascent hydrogen (Völker, *Deut. chem. Ges. Ber.*, viii. 1019). It boils at 135° (275° F.), its specific gravity at 0° (32° F.) being ·8335, and ·8188 at 20° (68° F.). By oxidation it yields ethylpropylketone, from which propionic and acetic acids are obtained by further oxidation.

Tertiary-butylmethylcarbinol; Pinacolic Alcohol: $C_4H_9^{\delta}.CH(CH_3).OH$, or $(CH_3)_3C.CH(CH_3).OH$.—Friedel and Silva have obtained this alcohol by the action of nascent hydrogen on pinacolin or tertiary-butylmethylketone (*Compt. Rend.*, lxxvi. 226); it is a liquid of camphorous odour, which boils at 120°·5 (248°·9 F.), and at 0° (32° F.) has the specific gravity ·8347. It solidifies at a low temperature to a mass of long silky needles, which melt at 4° (39°·2 F.). By careful oxidation it is reconverted into the ketone, which may be oxidized to trimethacetic acid:

$$(CH_3)_3C.CO.CH_3 + 4(O + OH_2) = (CH_3)_3C.COOH + H.COOH + 4H_2O.$$

This behaviour is of especial interest, as it is the only instance at present known in which, on oxidizing the ketone formed from a secondary alcohol of the ethylic series, the more complex radicle remains in combination with the CO group of the ketone, the simpler radicle being displaced by OH.

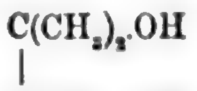
The constitution of this alcohol has been the subject of considerable discussion on account of its formation from pinacolin, which is produced by heating pinacone with dilute sulphuric acid; pinacone is a body obtained together with isopropylic alcohol when acetone is submitted to the action of nascent hydrogen, and its formation in this manner is the result of the following simple reaction:



$$\begin{array}{c} (CH_3)_2CO \\ \\ (CH_3)_2CO \end{array} + H_2 = \begin{array}{c} (CH_3)_2C.OH \\ | \\ (CH_3)_2C.OH \end{array}.$$

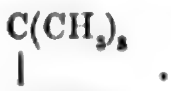
2 mols. acetone. Pinacone.

Pinacolin is produced from pinacone by the withdrawal of the elements of a molecule of water, but on comparing the formulæ of the two compounds, it will be obvious that its formation must be attended with isomeric change:



$$\begin{array}{c} C(CH_3)_2.OH \\ | \\ C(CH_3)_2.OH \end{array}$$

Pinacone.



$$\begin{array}{c} C(CH_3)_3 \\ | \\ CO.CH_3 \end{array}.$$

Pinacolin.

That this is the case there is no doubt, for Butlerow has shown that the ketone prepared from zincic methide and trimethacetic chloride, $C(CH_3)_3.COCl$, is identical with the pinacolin from acetone. The manner in which the conversion occurs cannot at present be traced, but it would appear to be an instance of *direct intramolecular change.*

(1444) *Tertiary Hexylic Alcohols.*—Three such are known, viz.:

		B.P. °C.
Methyldiethylcarbinol . .	$(C_2H_5)_2C(CH_3).OH$	119°—121°
Propyldimethylcarbinol .	$(CH_3)_2C(C_3H_7)^{\alpha}.OH$	114°—117°
Isopropyldimethylcarbinol .	$(CH_3)_2C(C_3H_7)^{\beta}.OH$	112°—113°

They are respectively obtained by the action of zincic ethide on acetic chloride, $CH_3.COCl$; by the action of zincic methide on butyric chloride, $C_3H_7{}^{\alpha}.COCl$; and by the action of zincic methide on isobutyric chloride, $C_3H_7{}^{\beta}.COCl$, the products of these reactions, after standing several days, being treated with water (Butlerow, *Jahrb.*, 1865, 461; Prianichnikoff, *Ann. Chem. Pharm.*, clxii. 67).

They are liquids possessing an alcoholic and camphorous odour. Diethylmethylcarbinol solidifies at − 35° (− 31° F.) to a mass of long fine needles, but the isomeric tertiary alcohols merely become viscid. On oxidation, diethylmethylcarbinol is converted into acetic acid; dimethylpropylcarbinol furnishes a mixture of propionic and acetic acids; and dimethylisopropylcarbinol yields acetone or dimethylketone. A small quantity of a hexylene was also formed from diethylmethylcarbinol.

(1445) HEPTYLIC ALCOHOLS: $C_7H_{15}.OH = 116$.—The nine following heptylic alcohols have been obtained:

		B.P. °C.
Hexylcarbinol	$C_6H_{13}{}^{\alpha}.CH_2.OH$	175°·5
Isoprimaryhexylcarbinol . . .	$C_6H_{13}{}^{\beta}.CH_2.OH$	163°—165°
Amylmethylcarbinol	$C_5H_{11}{}^{\alpha}.C(CH_3)H.OH$	160°—162°
Dipropylcarbinol	$(C_3H_7)_2{}^{\alpha}CH.OH$	149°—150°
Isoprimaryamylmethylcarbinol .	$C_5H_{11}{}^{\beta}.C(CH_3)H.OH$	146°—148°
Diisopropylcarbinol	$(C_3H_7)_2{}^{\beta}CH.OH$	131°—132°
Triethylcarbinol	$C_2H_5.C(C_2H_5)_2.OH$	140°—142°
Isoprimarybutyldimethylcarbinol	$C_4H_9{}^{\beta}.C(CH_3)_2.OH$	129°—131°
Tertiarybutyldimethylcarbinol .	$C_4H_9{}^{\delta}.C(CH_3)_2.OH$	131°—132°

(1446) *Primary Heptylic Alcohols. Normal Primary Heptylic Alcohol* or *Hexylcarbinol:* $C_6H_{13}{}^{\alpha}.CH_2(OH)$ or $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2(OH)$, is best prepared by the action of nascent hydrogen on heptylic or œnanthic aldehyde from castor oil, which for this purpose is dissolved in acetic acid and treated with sodium amalgam (Grimshaw and Schorlemmer, *Proc. Roy. Soc.*, 1873, 393): it may also be formed from normal heptane by chlorination, &c. It is a limpid, somewhat oily liquid, possessing an aromatic odour, and boils at 175°·5 (347°·9 F.) (Schorlemmer, *Ann. Chem. Pharm.*, clxxvii. 303); on oxidation it yields hexylic or œnanthic acid, $C_6H_{13}.COOH$.

Isoprimary or *β-Hexylcarbinol:* $(CH_3)_2CH.CH_2.CH_2.CH_2.CH_2(OH)$, is formed together with isoprimary or β-amylmethylcarbinol from the paraffin ethylisoamyl, $CH_3.CH_2.CH_2.CH_2.CH(CH_3)_2$, by Schorlemmer's method. It boils at 163°—165° (325°·4—329° F.), and on oxidation yields isoœnanthic acid, $(CH_3)_2CH.CH_2.CH_2.CH_2.COOH$ (Grimshaw, *Journ. Chem. Soc.*, xxvi. 313).

Schorlemmer has in a similar manner obtained an isomeric alcohol from the heptane which accompanies normal heptane in petroleum, but its constitution is not known; it boils at 165°—170° (329°—338° F.) (*ibid.*, 319).

According to Faget (*Ann. Chem. Pharm.*, cxxiv. 355), the portion of the fusel oil from the fermentation of grape skins, boiling at 155°—160° (239°—248° F.) has the composition of heptylic alcohol.

(1447) *Sec. Hept. Alcohols. Amylmethylcarbinol:* $C_5H_{11}{}^{\alpha}.C(CH_3)H.OH$, obtained from normal heptane, boils at 160°—162° (320°—323°·6 F.), and furnishes amylmethylketone on oxidation (Schorlemmer). The heptane which accompanies normal heptane yields an isomeric alcohol of unknown constitution, boiling at 148°—156° (298°·4—302° F.). The secondary alcohol, *isoamylmethylcarbinol:* $C_5H_{11}{}^{\beta}.C(CH_3)H.OH$, from the heptane ethylisoamyl, boils at 146°—148° (294°·8—298°·4 F.), and is converted into isoamylmethylketone by oxidation (Grimshaw).

Dipropylcarbinol: $C_3H_7{}^{\alpha}.C(C_3H_7)^{\alpha}H.OH$, is obtained by the action of nascent hydrogen on dipropylketone, $C_3H_7{}^{\alpha}.CO.C_3H_{7\alpha}$. It is a somewhat viscid liquid, of penetrating odour, only slightly soluble in water, and boiling at 149°—150° (300°·2—302° F.); its specific gravity at 25° (77° F.) is ·814. On oxidation, it is reconverted into the ketone (Kurtz, *Ann. Chem. Pharm.*, clxi. 212).

Diisopropylcarbinol, $C_3H_7{}^{\beta}.C(C_3H_7)^{\beta}H.OH$, is prepared in a similar manner from diisopropylketone, $C_3H_7{}^{\beta}.CO.C_3H_7{}^{\beta}$ (Münch, *ibid.*, clxxx. 333). It possesses a pleasant ethereal odour, somewhat like peppermint, and has the specific gravity ·8323 at 17° (62°·6 F.). It boils at 131°—132° (267°·8—269°·6 F.), and on oxidation is reconverted into the ketone.

(1448) *Tertiary Heptylic Alcohols. Triethylcarbinol:* $C_2H_5.C(C_2H_5)_2.OH$, prepared from propionic chloride, $C_2H_5.COCl$, and zincic ethide, is a colourless liquid of camphorous odour, difficultly soluble in water; it becomes viscid when cooled to − 20° (− 4° F.). It boils at 140°—142° (284°—287°·6 F.), and at 0° (32° F.) has the specific gravity ·8593. On treatment with an oxidizing mixture of sulphuric acid and potassic dichromate, it furnishes propionic and acetic acids, and a small quantity of a heptylene (Nahapetian, *ibid.*, clxii. 44).

Dimethylisobutylcarbinol: $C_4H_9{}^{\beta}.C(CH_3)_2.OH$, has been obtained from valeric chloride, $C_5H_{11}.COCl$, and zincic methide; the valeric acid employed in the preparation of the chloride being that produced by oxidizing fermentation amylic alcohol. The heptylic alcohol thus prepared is probably a mixture of isoprimary-butyldimethylcarbinol with small quantities of secondary-butyldimethylcarbinol. It is almost insoluble in water, and possesses a powerful camphorous odour; it boils at 129°—131° (264°·2—267°·8 F.). When cooled to − 20° (− 4° F.) it merely becomes viscid. On oxidation, it yields isobutyric and acetic acids (Pawloff, *ibid.*, clxxiii. 192).

Markownikoff, by combining the heptylene from oxyisocaprylic acid (p. 197) with hydriodic acid, and treating the resulting iodide with moist argentic oxide, obtained an alcohol boiling between 123° and 132° (253°·4 and 269°·6 F.), which there can be little doubt is impure isoprimary-butyldimethylcarbinol. It is distinguished by the readiness with which it is resolved into heptylene and water (*Zeits. Chem.*, 1871, 269).

Tertiary-butyldimethylcarbinol: $(CH_3)_3C.C(CH_3)_2.OH$, is obtained from trimethacetic chloride, $(CH_3)_3C.COCl$, and zincic methide. It crystallizes in long needles, melting at about 17° (62°·6 F.), and boils at about 131°—132° (267°·8—269°·6 F.); it attracts water with great avidity, forming a crystalline hydrate, $2C_7H_{16}O,H_2O$, which melts at about 83° (181°·4 F.). This hydrate crystallizes in long transparent prismatic needles, perceptibly soluble in water; it is extremely volatile even at ordinary temperatures, and especially on heating with water. It is very slowly acted upon by a mixture of potassic dichromate and dilute sulphuric acid; bromine is also without action at ordinary temperatures, but on warming a white solid product is obtained, which apparently is a mixture of $C_7H_{15}Br$ and $C_7H_{14}Br_2$ (Butlerow, *ibid.*, clxxvii. 176).

(1449) OCTYLIC ALCOHOLS: $C_8H_{17}.OH = 130$.—Our knowledge of these alcohols is at present very imperfect, only three being known with certainty, viz.:

		B.P. ° C.
Heptylcarbinol . . .	$C_7H_{15}{}^a.CH_2.OH$	196°—197°
Hexylmethylcarbinol .	$C_6H_{13}{}^a.C(CH_3).H.OH$	180°
Propyldiethylcarbinol .	$C_3H_7{}^a.C(C_2H_5)_2.OH$	?

(1450) *Normal Primary Octylic Alcohol* or *Heptylcarbinol*: $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2(OH)$, is obtained by saponifying the portion of the essential oil of *Heracleum spondylium*, boiling at 206°—208° (402°·8—406°·4 F.), and which chiefly consists of octylic acetate. Normal octylic ethers are also present in the oils from other *umbelliferæ*, such as *H. giganteum* and *Pastinaca sativa* (comp. Möslinger, *Deut. chem. Ges. Ber.*, ix. 998). It is a colourless, oily liquid, almost insoluble in water, of the specific gravity ·830 at 16° (60°·8 F.), and possesses a peculiar, penetrating, aromatic odour. It boils at 196°—197° (384°—386°·6 F.). On oxidation, it furnishes normal octylic or caprylic acid, $C_7H_{15}.COOH$ (Zincke, *Ann. Chem. Pharm.*, clii. 1; Renesse, *ibid.*, clxvi. 80).

(1451) *Primary-hexylmethylcarbinol*: $C_6H_{13}{}^a.C(CH_3)H.OH$. — This alcohol is obtained by the dry distillation of castor-oil soap. The corresponding ketone, methylhexylketone, is also produced; from Neison's experiments (*Journ. Chem. Soc.*, xxvii. 837), it appears that the ratio between the amount of alcohol and ketone depends upon the excess of alkaline hydrate and the temperature employed, a relatively greater yield of alcohol being obtained the higher the temperature, and the greater the excess of alkaline hydrate, within, of course, proper limits. A soap made from equal parts of sodium hydrate and castor-oil, with a quantity of water equal to about one-fourth the weight of the oil, may be employed, and distilled in quantities of 100 to 200 grammes from a copper retort.

Methylhexylcarbinol is a mobile, oily liquid, of peculiar aromatic odour, having the specific gravity ·823 at 16° (60°·8 F.); it boils at 181° (357°·8 F.) according to Neison, but according to Schorlemmer at 179°·5 (355°·1 F.) (*ibid.*, xxviii. 207). When oxidized it furnishes methylhexylketone, which on further oxidation is converted into acetic and normal caproic acids; bromine is readily dissolved by it, but exerts no action upon it at ordinary temperatures.

A mixture of this alcohol with the primary alcohol is obtained from normal octane by chlorination, &c. (Schorlemmer, *Ann. Chem. Pharm.*, clii. 152).

By distilling hexylmethylcarbinol with zincic chloride, combining the octylene thus obtained with hydriodic acid, converting the resulting octylic iodide into acetate by digesting it with argentic acetate, and saponifying this acetate, De Clermont has obtained an alcohol boiling at 174°—178° (345°·2—352°·4 F.), of the specific gravity ·811 at 0° (32° F.), and which furnishes methylhexylcarbinol and acetic and caproic acids on oxidation (*ibid.*, cxlix. 38; *Bull. Soc. Chim.* [2], xii.). Unless the action of zincic chloride on methylhexylcarbinol is attended with isomeric change, there can be little doubt that the octylene produced is a methylamylethylene of the formula $CH_3.CH{=}CH.C_5H_{11}{}^a$, and this olefine may be expected to furnish the iodide $CH_3.CHI.CH_2.C_5H_{11}{}^a$ when combined with hydriodic acid. The alcohol produced in the manner above described should, therefore, be methylhexylcarbinol; but, according to De Clermont, it does not agree with it in all it properties, although it furnishes the same oxidation products.

(1452) *Propyldiethlycarbinol:* $C_3H_7^a.C(C_2H_5)_2.OH$, is prepared from butyric chloride, $C_3H_7^a.COCl$, and zincic ethide, but it has not been obtained in a state of purity. Its boiling point is stated to be between 145° and 155° (293° and 311° F.), but these numbers are probably much too low; on oxidation it yields propionic and acetic acids (Butlerow, *Jahresb.*, 1865, 461).

(1453) *Higher Homologues of Ethylic Alcohol.*—No alcohols of known constitution of the higher terms of the series have been artificially prepared in a state of purity. What is probably a mixture of two nonylic alcohols has been obtained from petroleum nonane, and diisoamyl appears also to furnish a mixture of two isomeric decylic alcohols when chlorinated, &c. It is stated (*Deut. chem. Ges. Ber.*, v. 479) that when bromacetic bromide, $CH_2Br.COBr$, is submitted to the action of zincic ethide, and the product treated with water, a decylic alcohol, $C_{10}H_{21}.OH$, boiling at 155°—157° (311°—314°·6 F.) is obtained. The reaction is apparently of an altogether abnormal character and requires explanation: if a decylic alcohol is really produced, it is probably the tertiary alcohol $(C_2H_5)_2CH.C(C_2H_5)_2.OH$.

We have now only to consider the three remaining, and highest, terms of the series, which are derived from natural products—viz., *cetylic alcohol* or *ethal*, $C_{16}H_{33}.OH$; *cerylic alcohol*, $C_{27}H_{55}.OH$; and *melissic alcohol*, $C_{30}H_{61}.OH$.

Cetylic alcohol is prepared from spermaceti by saponification either by boiling it with an alcoholic solution of potassic hydrate, or by carefully fusing it with potassic hydrate; spermaceti consisting chiefly of cetylic palmitate. It is purified by crystallization from ether. Cerylic alcohol is obtained in a similar manner from Chinese wax or cerylic cerotate. Melissic alcohol is obtained by the action of melting potassic hydrate on myricin, the portion of bees-wax insoluble in boiling alcohol, and which consists chiefly of melissic palmitate.

These alcohols are crystalline waxy solids, insoluble in water, but soluble in ether and alcohol. Cetylic alcohol is stated to melt at 50° (122° F.), and to distil unaltered; cerylic alcohol melts at 97° (206°·6 F.), and is partly decomposed into water and cerotene, $C_{27}H_{54}$, on distillation; melissic alcohol melts at 85° (185° F.), and is also partially decomposed on distillation into water and melene, $C_{30}H_{60}$. When heated for some time with potassic hydrate these alcohols are converted into the potassic salts of the corresponding acids of the acetic series, for example:

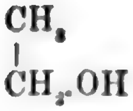
$$\underset{\text{Cetylic alcohol.}}{C_{16}H_{33}.OH} + KHO = \underset{\text{Potassic palmitate.}}{C_{16}H_{31}KO_2} + 2H_2.$$

From this behaviour they would appear to belong to the primary alcohols. At present no other reactions are known which tend to throw light upon their constitution.

(1454) In order to facilitate a comparison between the various homologous and isomeric alcohols of the ethylic series, they are classified in the following table in groups of strictly homologous compounds. The mean boiling point in ° C. is given for each alcohol underneath its formula:

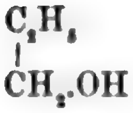
$CH_3.OH$

58°·6



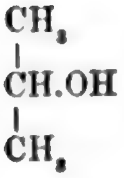
$\begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array}$

78°·4



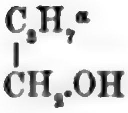
$\begin{array}{l} C_2H_5 \\ | \\ CH_2.OH \end{array}$

97°·4



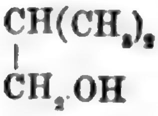
$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

82°·8



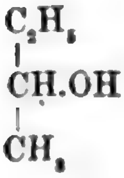
$\begin{array}{l} C_3H_7^{\alpha} \\ | \\ CH_2.OH \end{array}$

117°



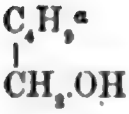
$\begin{array}{l} CH(CH_3)_2 \\ | \\ CH_2.OH \end{array}$

108°·4



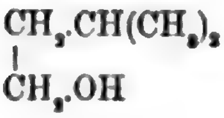
$\begin{array}{l} C_2H_5 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

99°



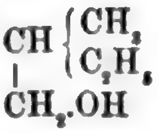
$\begin{array}{l} C_4H_9^{\alpha} \\ | \\ CH_2.OH \end{array}$

137°



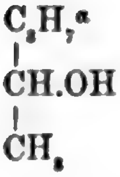
$\begin{array}{l} CH_2.CH(CH_3)_2 \\ | \\ CH_2.OH \end{array}$

131°



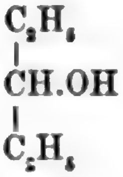
$\begin{array}{l} CH\left\{\begin{array}{l} CH_3 \\ C_2H_5 \end{array}\right. \\ | \\ CH_2.OH \end{array}$

128°



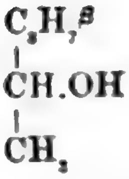
$\begin{array}{l} C_3H_7^{\alpha} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

120°



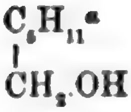
$\begin{array}{l} C_2H_5 \\ | \\ CH.OH \\ | \\ C_2H_5 \end{array}$

117°



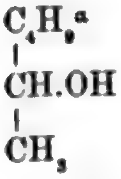
$\begin{array}{l} C_3H_7^{\beta} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

104°



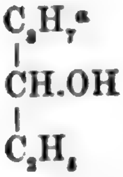
$\begin{array}{l} C_5H_{11}^{\alpha} \\ | \\ CH_2.OH \end{array}$

157°



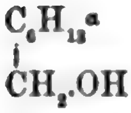
$\begin{array}{l} C_4H_9^{\alpha} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

138°



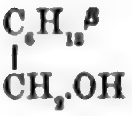
$\begin{array}{l} C_3H_7^{\alpha} \\ | \\ CH.OH \\ | \\ C_2H_5 \end{array}$

135°



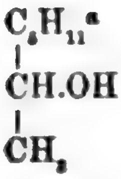
$\begin{array}{l} C_6H_{13}^{\alpha} \\ | \\ CH_2.OH \end{array}$

175°·5



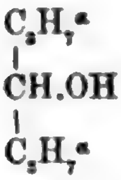
$\begin{array}{l} C_6H_{13}^{\beta} \\ | \\ CH_2.OH \end{array}$

164°



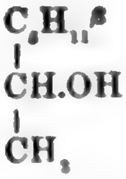
$\begin{array}{l} C_5H_{11}^{\alpha} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

161°



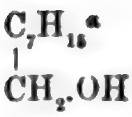
$\begin{array}{l} C_3H_7^{\alpha} \\ | \\ CH.OH \\ | \\ C_3H_7^{\alpha} \end{array}$

150°



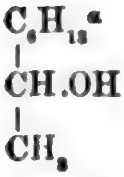
$\begin{array}{l} C_5H_{11}^{\beta} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

147°



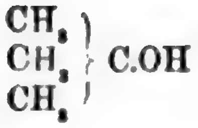
$\begin{array}{l} C_7H_{15}^{\alpha} \\ | \\ CH_2.OH \end{array}$

196°·5



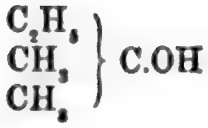
$\begin{array}{l} C_6H_{13}^{\alpha} \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$

180°



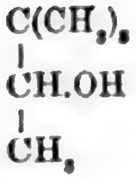
$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

82°·5



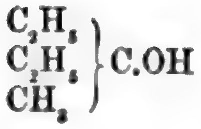
$$\left.\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

102°



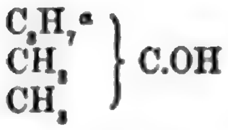
$$\begin{matrix}C(CH_3)_3\\|\\CH.OH\\|\\CH_3\end{matrix}$$

120°·5



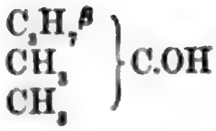
$$\left.\begin{matrix}C_2H_5\\C_2H_5\\CH_3\end{matrix}\right\}C.OH$$

120°



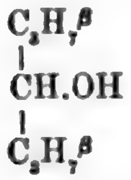
$$\left.\begin{matrix}C_3H_7\alpha\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

115°·0



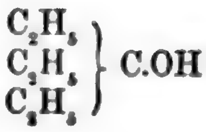
$$\left.\begin{matrix}C_3H_7\beta\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

112°·5



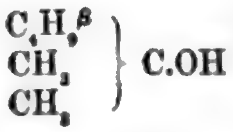
$$\begin{matrix}C_3H_7\beta\\|\\CH.OH\\|\\C_3H_7\beta\end{matrix}$$

131°·5



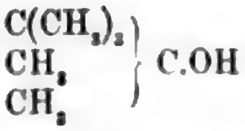
$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}C.OH$$

141°



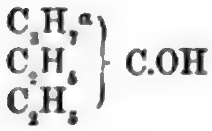
$$\left.\begin{matrix}C_4H_9\beta\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

130°



$$\left.\begin{matrix}C(CH_3)_3\\CH_3\\CH_3\end{matrix}\right\}C.OH$$

131°·5



$$\left.\begin{matrix}C_3H_7\alpha\\C_2H_5\\C_2H_5\end{matrix}\right\}C.OH$$

?

From this table it will be evident that a relation exists between the boiling points of the homologous alcohols; but this will be better seen on reference to the following table, which

B.P.	Dif.	B.P.	Dif.	B.P.	Dif.	B.P.	Dif.	B.P.	Dif.	B.P.	Dif.	B.P.	Dif.
58°·6													
	19°·8												
78°·4													
	19°·0												
97°·4				82°·8									
	19°·6				16°·2								
117°·0		108°·4		99°						82°·5			
	20°·0		22°·6		21°						19°·5		
137°·0		131°·0		120°		117°		104°		102°			
	20°·0		2 × 16°·5		18°		18°		2 × 21°·5		18°		
157°·0				138°		135°				120°		112°·5	
	18°·5				23°		15°				21°		17°·5
175°·5		164°·0		161°		150°		147°		141°		130°	
	21°·0				19°								
196°·5				180°									

exhibits only the boiling points of the alcohols, and the differences between them. In the series of normal primary alcohols the difference between the boiling points of two successive terms is in most cases 19°—20° C., 19°·7 being the mean difference in this group. The differences between successive terms in the other groups, it will be seen, also approximate more or less closely to this number, and the mean of the 23 differences in the table is 19°·2; hence it would seem that a difference in composition of CH_2 between two *strictly homologous* alcohols corresponds with a difference of 19° to 20° in boiling point; and it is the more probable that this relation obtains since the boiling points of most of the alcohols have been determined only approximately. Usually, only small quantities of material have been at the disposal of the operators, and therefore it has been impossible to completely purify the alcohols; moreover, the determinations have been made by different chemists, employing different instruments, and in most cases merely the observed boiling point is stated without correction. It is remarkable that whilst the difference in boiling point between successive homologues in the ethylic series of alcohols is apparently constant, and the same in each group, in the paraffin series of hydrocarbons quite a different relation obtains; thus we have seen (p. 133) that in the latter series, the increase of boiling point for each difference of CH_2 in the case of the normal paraffins diminishes progressively by about 4° from 37° to about 19°, when it appears to become constant. It will be evident, without further remark, from the table on the previous page, that if the relation in boiling point between the homologous alcohols of the ethylic series here pointed out as probable actually obtains, the boiling points of many of the alcohols are at present very incorrectly determined; for example, supposing that the boiling point of isoprimary-butylic alcohol is 108°·4 C., it is probable that 131° is too high a boiling point for the homologous isoprimary amylic alcohol, since the difference between the two numbers is no less than 22°·6. Similarly, if 82°·8 C. is the boiling point of isopropylic alcohol, that of the homologous ethylmethylcarbinol is probably 2° or 3° higher than 99°, since the difference between the numbers 82°·8 and 99° is only 16°·2.

(1455) *Haloid Derivatives of the Alcohols of the Ethylic Series.*—Very little is known in regard to the behaviour of the halogens with the alcohols of the ethylic series; chlorine and bromine appear to enter more or less readily into reaction with most of them, but it is doubtful whether iodine is capable of directly acting upon them.

Chlorine and bromine are without action on pure methylic alcohol in the cold (Henry, *Deut. chem. Ges. Ber.*, vi. 744; Grimaux, *Bull. Soc. Chem.*, 1874, xxii. 24); the nature of the products obtained on heating has yet to be ascertained.* To judge from the behaviour of ethylic alcohol and the few observations made with other primary alcohols, the first action of chlorine and bromine on primary alcohols consists in the displacement of one of the atoms of hydrogen attached to the carbon atom with which the OH group is associated; and if the behaviour of isopropylic alcohol is typical of that of secondary alcohols generally, the first product of the action of halogens on these alcohols is formed by the displacement of the atom of hydrogen associated with the carbon atom to which the OH group is united. The monohaloid derivatives thus produced are so unstable, however, that they cannot be isolated, being readily resolved into haloid acid and an aldehyde, if derived from a primary alcohol; or into haloid acid and a ketone, if derived from a secondary alcohol.

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* The statement on p. 425, that chlorine acts with great energy on methylic alcohol, is apparently incorrect. It was written without knowledge of Grimaux's experiments, which show that Cloez's observations were made with an impure alcohol containing acetone, and that the substances he obtained were derived from the latter, the so-called parachloride being pentachloracetone, $C_3H_1Cl_5O$, and parabromalide, pentabromacetone, C_3HBr_5O.

The continued action of the halogens on the primary alcohols does not lead to the displacement of a second atom of hydrogen in the $CH_2(OH)$ group, but chlorine or bromine becomes introduced in place of hydrogen in the radicle associated with this group. In the case of ethylic alcohol, we know that the whole of the hydrogen in this radicle may be displaced, and that the final product of the action of chlorine, for example, is the compound $CCl_3.CHCl.OH$, but we have no knowledge of the extent to which hydrogen may be displaced in other alcohols.

From the behaviour of trimethylcarbinol and of the so-called amylene hydrate, it appears that the tertiary alcohols may either furnish haloid derivatives which are more or less readily resolved into water and haloid olefine derivatives, or they are at once resolved into water and a dihaloid paraffin, the elements of a molecule of water apparently being directly split off, and displaced by a molecule of the halogen.

Monohaloid derivatives of alcohols are also obtained by the combination of the olefines with hypochlorous and hypobromous acids. In the compounds so formed, the halogen and the OH group are always attached to different, although contiguous, carbon atoms, and as compared with the monohaloid derivatives formed by the direct action of the halogens on primary and secondary alcohols, they are highly stable bodies. Thus monochlorethylic alcohol or glycolic chlorhydrin, $CH_2Cl.CH_2(OH)$, formed by the union of ethylene and hypochlorous acid, is a colourless liquid of specific gravity 1·24 at 8° (46°·4 F.), and boils at about 130° (266° F.); whilst the chloropropylic alcohol, $CH_3.CHCl.CH_2(OH)$, boils at about 128° (262°·4 F.). Very few, however, of these chlorinated alcohols have been prepared in a state of purity and their properties determined.

In discussing the law which regulates the combination of the olefines with hypochlorous acid (p. 401), we have stated that from Henry and Markownikoff's experiments it appears that propylene may combine with hypochlorous acid in the two ways represented by the following equations:

$$\alpha.\ CH_3.CH{=}CH_2 + Cl.OH = CH_3.CHCl.CH.OH.$$

$$\beta.\ CH_3.CH{=}CH_2 + Cl.OH = CH_3.CH(OH).CH_2Cl.$$

The first expresses the manner in which the reaction occurs, according to Henry; whilst the second represents Markownikoff's view. The experimental evidence from which these very opposite conclusions were drawn is derived from the study of the behaviour of the product on oxidation. Thus, to judge from the behaviour of propylic and isopropylic alcohols, a chloropropylic alcohol of the formula $CH_3.CHCl.CH_2(OH)$ may be expected to furnish the aldehyde, $CH_3.CHCl.COH$, on oxidation, and on further oxidation this should yield the chloropropionic acid, $CH_3.CHCl.COOH$; but chlorinated isopropylic alcohol, $CH_3.CH(OH).CH_2Cl$, should furnish monochloracetone, $CH_3.CO\,CH_2Cl$, which on further oxidation would yield acetic, carbonic, and hydrochloric acids.

By oxidizing the product with chromic acid mixture, Markownikoff obtained a body of the composition C_3H_5ClO, which on further oxidation furnished acetic, carbonic, and hydrochloric acids; he, therefore, concluded that monochloracetone was produced, and hence, that the product of the action of hypochlorous acid on propylene was the chlorinated alcohol, $CH_3.CH(OH).CH_2Cl$. Henry, however, found that when nitric acid was employed as oxidizing agent, the product was converted into the chloropropionic acid, $CH_3.CHCl.COOH$, thus proving apparently that it had the constitution expressed by the formula $CH_3.CHCl.CH_2(OH)$. Henry's more recent experiments (*Deut. chem. Ges. Ber.*, ix. 960, 1034) show that the different results obtained by Markownikoff and himself are probably due to the employment of a different oxidizing agent. Thus he finds that the chloropropionic acid, $CH_3.CHCl.COOH$, is oxidized by chromic acid to acetic and carbonic acids; the formation of these latter bodies, therefore, does not prove, as Markownikoff supposed it did, that the compound C_3H_5ClO, which he obtained, was monochloracetone, and not the isomeric chloropropionic aldehyde. The alcohol, $CH_3.CH(OH).CH_2Cl$, which Oppenheim obtained by the action of sulphuric acid on α-chloropropylene or allylic chloride (p. 204), when oxidized by nitric acid yields carbonic and monochloracetic acid, $CH_2Cl.COOH$, but chromic acid produces a small quantity of monochloracetone with acetic and carbonic acids.

Hence it would seem that the action of hypochlorous acid on the olefines does not vary, but that, as in the case of the haloid acids, its more negative constituent chlorine enters into union with the least hydrogenized carbon atom in the olefine, the less negative radicle OH combining with the contiguous carbon atom previously united by two affinities to that with which the chlorine becomes associated.

Two other methods of obtaining chloro- and bromo- derivatives of alcohols of the ethylic series remain to be mentioned. The first consists in acting upon polyhydric alcohols derived from paraffins with the haloid acids. Thus glycol is converted by hydrochloric acid into a monochlorethylic alcohol:

$$\underset{\text{Glycol.}}{CH_2(OH).CH_2(OH)} + HCl = \underset{\text{Chlorethylic alcohol.}}{CH_2Cl.CH_2(OH)} + OH_2,$$

and in a similar manner glycerin furnishes a dichlorisopropylic alcohol:

$$\underset{\text{Glycerin.}}{CH_2(OH).CH(OH).CH_2(OH)} + 2HCl = \underset{\text{Dichlorisopropylic alcohol.}}{CH_2Cl.CH(OH).CH_2Cl} + 2OH_2.$$

The chlorinated alcohols so produced are usually termed *chlorhydrins*, and the corresponding bromo-derivatives *bromhydrins*; since the halogen and OH are associated with different carbon atoms: they are stable compounds.

The second method consists in combining allylic alcohol with halogens. Thus, when combined with chlorine it forms a dichloropropylic alcohol:

$$\underset{\text{Allylic alcohol.}}{CH_2{=}CH.CH_2(OH)} + Cl_2 = \underset{\text{Dichloropropylic alcohol.}}{CH_2Cl.CHCl.CH_2(OH)}.$$

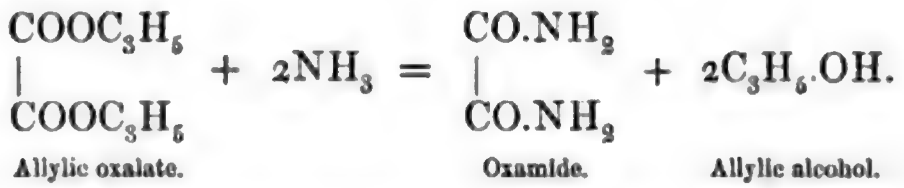
§ II. MONOHYDRIC ALCOHOLS OF THE $C_nH_{2n-1}.OH$ OR ALLYLIC SERIES.

Only three alcohols of this series are at present known to us: *Allylic alcohol,* $C_3H_5.OH$, *dimethylallylcarbinol,* $C_3H_5.C(CH_3)_2.OH$, and *menthylic alcohol* or *menthol,* $C_{10}H_{19}.OH$.

(1456) *Allylic Alcohol:* $C_3H_5.OH$ or $CH_2{=}CH.CH_2(OH)$.—This alcohol has only been artificially produced, but two of its derivatives may be obtained from natural sources—viz., allylic sulphide, $(C_3H_5)_2S$, which constitutes oil of garlic, and mustard oil or allylic isothiocyanate, $C_3H_5.NCS$. To procure the latter, bruised black mustard seed is macerated for some hours with water, and the mixture then distilled; it is formed by the decomposition of the potassic salt of an acid termed myronic acid under the influence of a ferment present in the seed, the potassic myronate being resolved into allylic isothiocyanate, dextroglucose and hydric potassic sulphate:

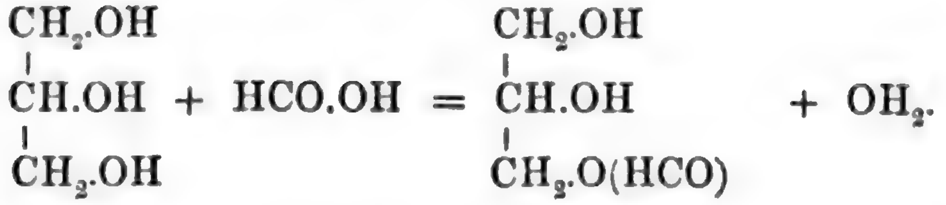
$$C_{10}H_{18}KNS_2O_{10} = C_3H_5.NCS + C_6H_{12}O_6 + KHSO_4.$$

Allylic alcohol is produced when acroleïn or acrylic aldehyde, C_3H_4O, is submitted to the action of zinc and hydrochloric acid (Linnemann; Claus, *Deut chem. Ges. Ber.*, iii. 404). It may be obtained from the allylic iodide from glycerin, which for this purpose is converted into allylic oxalate by treatment with argentic oxalate, and the oxalate so produced decomposed by ammonia gas:



$$\underset{\text{Allylic oxalate.}}{\begin{array}{l}COOC_3H_5\\ |\\ COOC_3H_5\end{array}} + 2NH_3 = \underset{\text{Oxamide.}}{\begin{array}{l}CO.NH_2\\ |\\ CO.NH_2\end{array}} + \underset{\text{Allylic alcohol.}}{2C_3H_5.OH.}$$

Allylic alcohol is now always prepared, however, according to Tollens and Henninger's method, by heating glycerin with oxalic acid (*Ann. Chem. Pharm.*, clvi. 134). In this process, the oxalic acid is decomposed on heating into carbonic anhydride and formic acid: $H_2C_2O_4 = CO_2 + H.COOH$; the latter entering into reaction with the glycerin, produces an acid glyceric formate or monoformin, which on distillation is resolved into allylic alcohol, water and carbonic anhydride:



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + HCO.OH = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.O(HCO) \end{array} + OH_2.$$

Glycerin. Monoformin.

$$CH_2(OH).CH(OH).CH_2(O.HCO) = CH_2(OH).CH{=}CH_2 + CO_2 + OH_2.$$

Glyceric monoformate. Allylic alcohol.

The mixture of 4 pts. of glycerin and 1 pt. of oxalic acid is heated in a retort provided with a thermometer and connected with a condenser, the receiver being changed when the temperature rises to 195° (383° F.), and the distillation continued from that point to 260° (500° F). The presence of an alkaline-metal salt in the oxalic acid, unless of a stronger acid, greatly interferes with the production of the alcohol, and appears to promote in a remarkable manner the decomposition of the formic acid into carbonic oxide and water; therefore, when commercial oxalic acid is employed, about half a per cent. of sodic chloride and a quarter to one-half a per cent. of ammonic chloride is added. If after heating to 260° (500° F.) the liquid has still an alkaline reaction, too little, but if the glycerin darkens much on heating, too much ammonic chloride is present. If the operation be successful a peculiar, somewhat irritating, but highly characteristic odour is developed, and oily streaks appear in the neck of the retort; if these indications are not observed when the temperature has risen to 215°—220° (419°—428° F.) a small quantity of ammonic chloride is added. The distillate is a mixture of allylic alcohol with water and some allylic formate, glycerin and glyceric allylic ether, sometimes with much acroleïn. The excess of glycerin remaining in the retort serves to convert fresh quantities of oxalic acid. To obtain the alcohol the distillate is rectified until oily drops no longer separate on the addition of potassic carbonate to the liquid which passes over; this is usually the case when the thermometer registers about 105° (221° F.). The crude alcohol is separated from this distillate by the addition of potassic carbonate, it is then dried over potassic carbonate, allowed to stand for 24 hours in contact with 5 to 10 per cent. of pulverized potassic hydrate, rectified and freed from the last traces of water by digestion with anhydrous baryta. In this manner an amount of allylic alcohol may be obtained equal to about 20 per cent. of the weight of the oxalic acid employed.

Allylic alcohol is a colourless liquid of sharp irritating odour, miscible in all proportions with water; it boils at 96°—97° (204° 8—206°·6 F.), and at 0° (32° F.) has the specific gravity ·8709. When cooled to −50° (−58° F.) it solidifies. It is converted by nascent hydrogen into propylic alcohol, but the conversion is only imperfectly effected by the employment of either sodium amalgam and water, or zinc and hydrochloric or sulphuric acid; the tendency to combine with hydrogen appears, however, to be far greater in acid than alkaline solutions (Linnemann, *Deut. chem. Ges. Ber.*, vii. 854). When allylic alcohol is heated with solid potassic hydrate it also furnishes propylic alcohol, but the reaction is complicated by the occurrence of secondary reactions, as besides oily substances, ethylic alcohol, formic acid, and probably propionic acid, are produced. The mixture of equal weights of the two substances, placed in a flask attached to a condenser, is heated in an oil bath: the reaction commences at about 100° (212° F.), and by the time that the temperature of the bath has been carefully raised to 155° it is almost complete (Tollens, *Ann. Chem. Pharm.*, clix. 92). In the purification of the crude alcohol from glycerin, it is on this account necessary to avoid heating with potassic hydrate. On adding allylic alcohol to an oxidizing mixture of dilute sulphuric acid and potassic dichromate, a powerful odour of acroleïn is developed and carbonic anhydride escapes, but on afterwards distilling the liquid only formic acid is obtained; with nitric acid, formic and oxalic acids are produced.

Allylic alcohol readily exchanges OH for Cl, Br or I when submitted to the action of the haloid acids and haloid phosphorus compounds, and it reacts with sulphuric acid to form hydric allylic sulphate, $C_3H_5.HSO_4$; sodium dissolves in it with evolution of hydrogen, producing sodic allylate, $C_3H_5.ONa$. Allylic alcohol in this respect resembles the alcohols of the ethylic series, but it differs from them by combining directly with chlorine, bromine, cyanogen, &c., forming the compounds $C_3H_5Cl_2.OH$, $C_3H_5Br_2.OH$ and $C_3H_5(CN)_2.OH$. The alcohol is readily reproduced from its compounds with the halogens by the action of nascent hydrogen, but it then contains traces of propylic alcohol (Linnemann, *loc. cit.*). The compound with bromine yields *dibromopropionic acid*, $C_2H_3Br_2.COOH$, on oxidation with nitric acid.

The constitution of allylic alcohol has recently been the subject of much discussion, with the result, however, that chemists generally now regard the formula $CH_2{=}CH.CH_2(OH)$ as the only one by which its reactions can be satisfactorily expressed. The alternative formula $CH_3.CH{=}CH(OH)$ would require the formation of acetic acid on oxidation; moreover, the supposition of the existence of the CH_3 group in allylic alcohol is altogether irreconcilable with the facts that allylic bromide combines with bromine to form a tribromopropane identical with the so-called tribromhydrin from glycerin, and that when allylic bromide is combined with hydrobromic acid it furnishes a dibromopropane (p. 160), which is not identical with ordinary propylene bromide, $CH_3.CHBr.CH_2Br$, but has a higher boiling point (comp. Wislicenus, *Ann. Chem. Pharm.*, clxvi. 45; Tollens, *ibid.*, clxvii. 257).

(1457) *Allyldimethylcarbinol:* $C_3H_5.C(CH_3)_2.OH$, is produced by the action of zinc on a mixture of allylic iodide and dimethylketone, and subsequently treating the product with water; it boils at 119° (246°·2 F.) (Saytzeff, *Deut. chem. Ges. Ber.*, ix. 33).

(1458) *Menthylic Alcohol* or *Menthol:* $C_{10}H_{19}.OH$.—This substance is deposited in crystals when essential oil of peppermint is cooled to a low temperature; it is now imported in large quantities from Japan. The Japanese camphor, according to Beckett and Wright (*Journ. Chem. Soc.*, xxix. 1), separates from alcohol as an oil which crystallizes on exposure to air; the crystals melt at 42° (107°·6 F.) and boil at 212° (413°·6 F.)

Menthol is but slightly soluble in water, but imparts to it a strong fragrant aromatic smell and taste; it is very soluble in alcohol, ether, and oils, but insoluble in aqueous alkalies. It crystallizes from an alcoholic solution of sodic hydrate in long needles. It is converted into the compound $C_{10}H_9Cl$ or menthylic chloride when heated for a considerable time with a concentrated solution of hydrochloric acid, or by phosphoric pentachloride; corresponding bromine and iodine compounds are formed by the action of the bromide and iodide of phosphorus. Sodium acts very energetically upon menthol, with evolution of hydrogen. When distilled with zincic chloride it yields menthene, $C_{10}H_{18}$ (1258).

§ III. MONOHYDRIC ALCOHOLS OF THE $C_nH_{2n-3}.OH$ AND $C_nH_{2n-5}.OH$ SERIES.

(1459) The lowest term of the $C_nH_{2n-3}.OH$ series is *propargylic alcohol,* $C_3H_3\,OH$. Probably some of the oxidized oils of the composition $C_{10}H_{18}O$ which accompany terpenes in the essential oils of various plants are members of this series—viz., bodies such as *citronellol* from the essential oil of citronella (*Andropogon Schœnanthus*), *absinthol* from oil of wormwood, and *cajeputol* from oil of cajeput. At present, however, we are almost entirely unacquainted with the properties of these bodies.

Similarly, *myristicol,* $C_{10}H_{16}O$, from oil of nutmeg, is probably an alcohol of the $C_nH_{2n-5}.OH$ series, since it exchanges OH for Cl when submitted to the action of phosphoric pentachloride (Wright, *Chem. Soc. Journ.*, xxvi. 687).

(1460) *Propargylic Alcohol:* $C_3H_3.OH$ or $CH{\equiv}C.CH_2(OH)$.—To prepare this alcohol, bromallylic acetate (p. 206) is saponified by treatment with solid potassic hydrate at ordinary temperatures, or by distillation from pieces of sodic hydrate; it is thus converted into bromallylic alcohol:

$$\underset{\text{Bromallylic acetate.}}{CH_2{=}CBr.CH_2(C_2H_3O_2)} + KHO = \underset{\text{Bromallylic alcohol.}}{CH_2{=}CBr.CH_2(OH)} + KC_2H_3O_2,$$

which is a colourless mobile liquid of pleasant odour, boiling at 155° (311° F.) (Henry, *Deut. chem. Ges. Ber.*, v. 453). When heated with the necessary quantity of potassic hydrate and a small quantity of water it is converted into propargylic alcohol:

$$\underset{\text{Bromallylic alcohol.}}{CH_2{=}CBr.CH_2(OH)} + KHO = \underset{\text{Propargylic alcohol.}}{CH{=}C.CH_2(OH)} + KBr + OH_2.$$

Propargylic alcohol is a colourless mobile liquid of pleasant odour, soluble in water; it boils at 114°—115° (237°·2—239° F.), and at 21° (69°·8 F.) has the specific gravity ·96. It exhibits the property so characteristic of many of the hydrocarbons of the acetylene series of forming metallic derivatives. Thus, when it is added to an ammoniacal solution of cuprous chloride a canary-yellow coloured precipitate of the composition $(C_3H_2.OH)_2Cu_2$ is thrown down, and a white precipitate of the composition $C_3H_2Ag.OH$ is produced when it is added to an ammoniacal solution of argentic nitrate; these substances burn explosively when ignited. When the alcohol is heated with potassic hydrate it readily furnishes acetylene, hydrogen, and potassic formate:

$$CH \equiv C.CH_2(OH) + KHO = HC \equiv CH + H_2 + H.COOK.$$

Propargylic alcohol combines readily with bromine and with the haloid acids, so that its haloid derivatives cannot be produced by the action of the latter on the alcohol; they are obtained, however, by acting upon it with the haloid phosphorus compounds. Propargylic chloride or monochlorallylene, $CH \equiv C.CH_2Cl$, is a very mobile liquid, of extremely pleasant odour, insoluble in water; it boils at 65° (149° F.), and at 5° (41° F.) has the specific gravity 1·0454. The bromide, $CH \equiv C.CH_2Br$, boils at 88°—90° (190°·4—194° F.), and at 11° (51°·8) has the specific gravity 1·59; it combines with bromine, forming the compounds $CHBr = CBr.CH_2Br$ and $CHBr_2.CBr_2.CH_2Br$, which cannot be distilled. The iodide, $CH \equiv C.CH_2I$, is a white crystalline substance, which melts at about 49° (120°·2 F.), but cannot be distilled (Henry, *ibid.*, v. 570; vii. 761; viii. 398).

(1461) *Diallylmethylcarbinol:* $CH_3.C(C_3H_5)_2.OH$, is produced by the action of zinc on a mixture of allylic iodide and ethylic acetate, and treating the product with water; it boils at 157° (314°·6 F.) (Saytzeff, *ibid.*, ix. 34).

§ IV. MONOHYDRIC ALCOHOLS OF THE $C_nH_{2n-7}.OH$ SERIES.

These alcohols bear the same relation to the hydrocarbons of the benzene series that the monohydric alcohols of the ethylic series bear to the paraffins. But the series includes two groups possessing very dissimilar properties: the so-called *phenols* or alcohols derived from hydrocarbons of the benzene series by the displacement of an atom of hydrogen in the C_6 group by the group OH; and the compounds, which for want of a better name may be called *alcohols of the benzylic series*, formed by the displacement of hydrogen in the so-called side-chain of the hydrocarbon. The two classes of alcohols are represented by the following general formulæ :

$C_6H_{6-m}(C_nH_{2n+1})_m$* ;	$C_6H_{5-m}(OH).(C_nH_{2n+1})_m$;	$C_6H_{5-m}\left\{\begin{array}{l}C_nH_{2n}.OH\\ C_nH_{2n+1})_{m-1}\end{array}\right.$
Hydrocarbon of benzene series.	Phenol.	Alcohol of benzylic series.

Each of these groups of *metameric* compounds may include numerous isomerides. Like the hydrocarbons from which they are derived, these alcohols exhibit the behaviour of saturated compounds, but to a far more pronounced extent, as, so far as we are at present aware, they do not under any circumstances furnish stable additive compounds. In their general behaviour the alcohols of the benzylic series very closely resemble the alcohols of the ethylic series, but the phenols possess totally distinct properties.

(1462) The following monohydric alcohols derived from hydrocarbons of the benzene series are known :

			B.P. °C.
C_6H_6O	Phenol or Oxybenzene	$C_6H_5.OH$	182°
C_7H_8O	Benzylic alcohol or Phenylcarbinol . . .	$C_6H_5.CH_2(OH)$	207°
	Paracresol or Paroxymethylbenzene . . .	$CH_3.C_6H_4.OH$	198°
	Metacresol or Metoxymethylbenzene . .		200°
	Orthocresol or Orthoxymethylbenzene . .		186°
$C_8H_{10}O$	Paratolylic alcohol or Tolylcarbinol . .	$CH_3.C_6H_4.CH_2(OH)$	217°
	Primary phenylethylic alcohol	$C_6H_5.CH_2.CH_2(OH)$	212°
	Secondary phenylethylic alcohol or Methylphenylcarbinol	$CH_3.CH(C_6H_5).OH$	203°
	Metaxenol or Oxymetadimethylbenzene .	$(CH_3)_2C_6H_3.OH$	215°
	Xenol (liquid) (?) Oxyparadimethylbenzene		212°
	Ethylphenol (solid) (?) Paroxyethylbenzene	$C_2H_5.C_6H_4.OH$	214°
	Ethylphenol(liquid)(?)Orthoxyethylbenzene		212°
	Phlorol Oxyethylbenzene		220°
$C_9H_{12}O$	Primary phenylpropylic alcohol	$C_6H_5.CH_2.CH_2.CH_2(OH)$	235°
	Secondary phenylpropylic alcohol or Ethylphenylcarbinol	$C_2H_5.CH(C_6H_5).OH$	210°
	Mesitol or Oxymesitylene	$(CH_3)_3C_6H_2$ OH	?
$C_{10}H_{14}O$	Cuminylic alcohol	$C_3H_7.C_6H_4.CH_2(OH)$	243°
	Secondary phenylbutylic alcohol or Propylphenylcarbinol	$C_3H_7.CH(C_6H_5).OH$	230°
	Thymol or α-Oxyparamethylpropylbenzene	$C_6H_3(OH)\left\{\begin{array}{l}CH_3\\ C_3H_7\end{array}\right.$	233°
	Carvacrol or β-Oxyparamethylpropylbenzene		
$C_{18}H_{30}O$	Sycocerylic alcohol	$C_{18}H_{29}.OH$	—

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[*] The value of *m* may be 0, and cannot exceed 6 ; where there are several C_nH_{2n+1} groups in the hydrocarbon *n* may have the same or a different value in each.

(1463) *Methods of Preparing Phenols.*—The phenols cannot be obtained from the mono-haloid derivatives of the hydrocarbons of the benzene series in which the halogen is associated with the C_6 group, potassic hydrate, argentic acetate, &c., being entirely without action on these compounds; but they are prepared by a method which in principle is the same as that by which the alcohols of the ethylic series are formed from the paraffins. This consists in converting the hydrocarbon by the action of concentrated sulphuric acid into a mono-sulphonic acid, and carefully fusing the potassic salt of this acid with about twice its weight of potassic hydrate; thus:

$$\underset{\text{Benzene.}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5.SO_3H} + OH_2.$$

$$\underset{\text{Potassic benzenesulphonate.}}{C_6H_5.SO_3K} + KHO = \underset{\text{Phenol.}}{C_6H_5.OH} + K_2SO_3.$$

The operation is one requiring great care, and the amount of phenol produced is always much below the theoretical quantity. The fusion should be conducted at as low a temperature as possible in a silver or iron dish, and the mass constantly stirred in order to avoid secondary reactions; the heating is continued until it is ascertained, by taking out small portions from time to time and adding acid, that the amount of phenol formed does not increase. The phenols are obtained by dissolving the fused mass in water and supersaturating the solution with hydrochloric or sulphuric acid; the oil which rises to the surface may easily be separated, but as most of the phenols are soluble to some extent in water, the solution should be agitated with ether to extract the dissolved phenol. In order to free the crude phenol from the acids with which it is frequently contaminated, and which are produced by the oxidizing action of the potassic hydrate, it is shaken with a saturated solution of ammonic carbonate, by which the acids are dissolved. It is then often advisable to distil the phenol in a current of steam before it is finally purified by distillation alone. On account of their high boiling points the phenols can usually be dehydrated by simple distillation; it is seldom desirable to employ desiccating agents, but exposure over sulphuric acid in vacuo may be advantageously resorted to in some instances as a means of removing the water.

The second general method of preparing phenols is similar in principle to that by which the alcohols of the ethylic series are prepared from the corresponding amines. The hydrocarbon of the benzene series corresponding to the phenol required is converted by the action of concentrated nitric acid into the mononitro-derivative, which is then reduced by tin and hydrochloric acid, or some other suitable reducing agent, to the amido-derivative or amine; a salt, usually the nitrate, of this amine is then submitted to the action of nitrous acid, being for this purpose either suspended or dissolved in anhydrous alcohol; the diazo-nitrate thus produced is converted by treatment with sulphuric acid into the corresponding sulphate, and finally this salt is decomposed by heating with water. For example:

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + H_2O.$$

$$\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + 3H_2 = \underset{\text{Amidobenzene.}}{C_6H_5.NH_2} + 2H_2O.$$

$$\underset{\text{Amidobenzene nitrate.}}{C_6H_5.NH_3(NO_3)} + HNO_2 = \underset{\text{Di zobenzene nitrate.}}{C_6H_5.N_2(NO_3)} + 2OH_2.$$

$$\underset{\text{Diazobenzene sulphate.}}{C_6H_5.N_2(HSO_4)} + OH_2 = \underset{\text{Phenol.}}{C_6H_5.OH} + N_2 + H_2SO_4.$$

A third method of obtaining phenols is by distilling oxy-acids such as salicylic acid, $C_6H_4(OH).COOH$, and oxyuvitic acid, $CH_3.C_6H_2(OH)(COOH)_2$, with lime or baryta, and thereby abstracting the elements of one or more molecules of carbonic anhydride.

(1464) *Methods of Preparing Alcohols of the Benzylic Series.*—There are three methods of general application, which are precisely analogous to those by which alcohols of the ethylic series are prepared: 1. The monohaloid derivatives of the hydrocarbons of the benzene series prepared by the action of the halogens on the heated hydrocarbons, that is to say, those which contain the halogen in the side-chain, are converted by treatment with potassic acetate into the corresponding acetate, which is then saponified; thus:

$$\underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} + KC_2H_3O_2 = \underset{\text{Benzylic acetate.}}{C_6H_5.CH_2(C_2H_3O_2)} + KCl.$$

$$\underset{\text{Benzylic acetate.}}{C_6H_5.CH_2(C_2H_3O_2)} + KHO = \underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2(OH)} + KC_2H_3O_2.$$

2. The aldehydes of the benzoic series are heated with an alcoholic solution of potassic hydrate; a portion of the aldehyde is thus converted into the corresponding acid of the benzoic series, and the hydrogen which this transformation furnishes, converts another portion of the aldehyde into the alcohol. In this manner only primary alcohols are formed. For example:

$$\underset{\text{Benzoic aldehyde.}}{C_6H_5.COH} + KHO = \underset{\text{Potassic benzoate.}}{C_6H_5.COOK} + H_2.$$

$$\underset{\text{Benzoic aldehyde.}}{C_6H_5.COH} + H_2 = \underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2(OH)}.$$

3. Lastly, secondary alcohols of the benzylic series are pro-

duced by the action of nascent hydrogen on the ketones of the form $C_nH_{2n-7}.CO.C_nH_{2n+1}$; thus:

$$C_nH_{2n-7}.CO.C_nH_{2n+1} + H_2 = C_nH_{2n-7}.CH(OH).C_nH_{2n+1}.$$

$$\underset{\text{Methylphenylketone.}}{C_6H_5.CO.CH_3} + H_2 = \underset{\text{Methylphenylcarbinol.}}{C_6H_5.CH(OH).CH_3.}$$

(1465) *General Properties of the Phenols and Alcohols of the Benzylic Series.*—1. The haloid acids are without action upon the phenols, but readily convert the alcohols of the benzylic series into the corresponding haloid hydrocarbon derivatives:

$$\underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2(OH)} + HCl = \underset{\text{Benzylic chloride.}}{C_6H_5.CH_2Cl} + OH_2.$$

The corresponding haloid derivatives may be obtained from the phenols, however, by the action of phosphoric pentachloride or pentabromide:

$$\underset{\text{Phenol.}}{C_6H_5.OH} + PCl_5 = \underset{\text{Chlorobenzene.}}{C_6H_5Cl} + POCl_3 + HCl.$$

The phosphoric oxychloride thus produced at once acts upon another portion of the phenol forming the corresponding phosphate:

$$POCl_3 + \underset{\text{Phenol.}}{3C_6H_5.OH} = \underset{\text{Phenylic phosphate.}}{PO(OC_6H_5)_3} + 3HCl.$$

2. The phenols readily dissolve in, and enter into reaction with, concentrated sulphuric acid, forming sulphonic acids, but the alcohols of the benzylic series are resinified by treatment with the concentrated acid:

$$\underset{\text{Phenol.}}{C_6H_5.OH} + H_2SO_4 = \underset{\text{Phenolsulphonic acid.}}{C_6H_4(OH).SO_3H} + OH_2.$$

3. On oxidation, the alcohols of the benzylic series behave precisely as the alcohols of the ethylic series, the $CH_2.OH$ group of the primary alcohols being oxidized to COOH, and the CH.OH group of the secondary alcohols to CO; but it is necessary to effect the oxidation with extreme care, as the entire side-chain is liable to undergo oxidation in the manner characteristic of the hydrocarbons of the benzene series. The phenols behave in an entirely different manner, and mostly furnish *quinones*; probably, however, the first product of oxidation is a hydroquinone or dihydric alcohol of the $C_nH_{2n-8}(OH)_2$ series, which on further oxidation is converted into the quinone, thus:

$$C_6H_5.OH + (O+OH_2) = C_6H_4(OH)_2 + OH_2$$

Phenol. Hydroquinone.

$$C_6H_4(OH)_2 + (O+OH_2) = C_6H_4O_2 + 2OH_2.$$

Quinone.

Since the hydroquinones are formed by the displacement of an atom of hydrogen in the phenol which occupies the para-position relatively to the OH group, only those homologues of phenol furnish quinones on oxidation in which the para-position is not occupied by a side-chain; the behaviour of phenols which do not come within this definition is not known, but probably they will be found to furnish oxyacids through the oxidation of the side-chains to COOH. All the homologues of phenol behave in this manner, that is to say, the side-chains are oxidized to COOH, when heated with fused potassic hydrate; thus the three isomeric cresols furnish the potassic salts of the corresponding oxybenzoic acids when fused with potassic hydrate:

$$C_6H_4(OH).CH_3 + 2KHO = C_6H_4(OK).COOK + 3H_2.$$

Cresol. Dipotassic salt of oxybenzoic acid.

The ethers formed by displacing the hydrogen in the OH group by methyl or ethyl are similarly oxidized by the ordinary reagents, such as chromic acid and potassic permanganate, and afford most important aid in the investigation of the constitution of the phenols; for example, the methylic ethers derived from the cresols are readily converted into corresponding methoxybenzoic acids on oxidation:

$$C_6H_4(OCH_3).CH_3 + 3(O+OH_2) = C_6H_4(OCH_3).COOH+4OH_2.$$

Cresylmethylether. Methoxybenzoic acid.

4. The phenols are mostly converted by the action of nitric acid into well characterized nitro-derivatives, thus:

$$C_6H_5.OH + HNO_3 = C_6H_4(NO_2).OH + OH_2;$$

Phenol. Nitrophenol.

but the alcohols of the benzylic series are oxidized by this reagent, benzylic alcohol, $C_6H_5.CH_2(OH)$, being converted into benzoic aldehyde, $C_6H_5.COH$, and ultimately into benzoic acid.

5. The monohydric alcohols derived from benzene, like the alcohols of the ethylic series, furnish metallic derivatives, dissolving sodium and potassium with evolution of hydrogen:

$$2C_6H_5.OH + 2Na = C_6H_5.ONa + H_2.$$

Phenol. Sodium phenol.

But the phenols dissolve readily even in aqueous solutions of the alkaline hydrates; moreover their metallic derivatives are exceedingly stable as compared with those of the alcohols of the ethylic series, and may in many instances be recovered from their aqueous solutions by evaporation. On account of this behaviour the phenols are often spoken of as acids, phenol itself having long received the name of carbolic acid. It is to be noticed that the acid properties of the phenols become less pronounced as the series is ascended; on the other hand, the introduction of negative radicles such as the halogens and (NO_2) renders them more pronounced. Thus the higher haloid and the nitro-derivatives of the phenols not only dissolve in aqueous solutions of the alkaline hydrates, but they decompose the metallic carbonates with effervescence forming corresponding metallic derivatives.

One of the most characteristic properties of the potassium and sodium derivatives of the phenols is their power to enter directly into combination with carbonic anhydride, forming salts of the corresponding oxy-acids. For example, when sodium phenol is heated in an atmosphere of carbonic anhydride disodium salicylate is produced and phenol distils over:

$$\underset{\text{Sodium phenol.}}{2C_6H_5.ONa} + CO_2 = \underset{\text{Disodium salicylate.}}{C_6H_4(ONa).COONa} + \underset{\text{Phenol.}}{C_6H_5.OH}.$$

The reaction, however, probably occurs in two stages, a disodium phenol being first produced from two molecules of the sodium phenol:

$$\underset{\text{Sodium phenol.}}{C_6H_5.ONa} + \underset{\text{Sodium phenol.}}{C_6H_5.ONa} = \underset{\text{Disodium phenol.}}{C_6H_4Na.ONa} + \underset{\text{Phenol.}}{C_6H_5.OH};$$

which at the moment of formation enters into reaction with the carbonic anhydride.

$$\underset{\text{Disodium phenol.}}{C_6H_4Na(ONa)} + CO_2 = \underset{\text{Disodium salicylate.}}{C_6H_4(ONa).COONa}.$$

6. When distilled over heated zinc dust the phenols are converted into the corresponding hydrocarbons of the benzene series; for example:

$$\underset{\text{Phenol.}}{C_6H_5.OH} + Zn = \underset{\text{Benzene.}}{C_6H_6} + ZnO.$$

7. Many of the phenols and of their derivatives when mixed with a solution of ferric chloride produce characteristic colours; phenol, for example, furnishes a violet solution.

(1466) PHENOL. *Oxybenzene, Phenylic Hydrate* or *Carbolic Acid:* $C_6H_5.OH = 94$.—Phenol may be obtained by the general methods above described from benzene and the oxybenzoic acids, and it is also formed in small quantity, together with glyceric ether and other products, when glycerin is distilled with calcic chloride (Linnemann and von Zotta, *Ann. Chem. Pharm. Sup.*, viii. 254). It appears also to be produced when glycerin is heated with other dehydrating agents such as zincic chloride and hydric potassic sulphate, and by the action of a concentrated solution of potassic hydrate on glyceric ether, $(C_3H_5)_2O_3$. According to Berthelot, by heating acetylene with fuming sulphuric acid it is converted into acetylenesulphonic acid, $C_2H.SO_3H$, and on fusing the potassic salt of this acid with potassic hydrate phenol is obtained (*Compt. Rend.*, lxviii. 539). The chief source of phenol, however, is coal-tar, from which it may be prepared in the following manner:

By treating light coal-tar naphtha, or the portion of coal-tar oil boiling at about 150°—200° (302°—392° F.), with a solution of sodic hydrate or milk of lime, all the acid substances present and a not inconsiderable quantity of naphthalene are dissolved; much of the naphthalene is precipitated on diluting with water, and if the solution be then exposed to the air in shallow vessels for several days it turns dark brown, and certain impurities are thus removed by oxidation. The acid substances present in this solution consist of phenol and its homologues and bodies of unknown composition, but phenol appears to possess more pronounced acid properties than any of the bodies with which it is associated; hence, on adding insufficient acid to precipitate the whole of the acid compounds, chiefly phenol remains in solution, so that by the addition of successive quantities of sulphuric acid the greater part of the impurities are removed, and the oil which finally separates on supersaturating the solution with acid is comparatively pure phenol. It is further purified by fractional distillation, and the portion which comes over a few degrees below and above 182° (359°·6 F.) is well cooled; it then solidifies to a mass of crystals, from which the liquid portion is removed by draining and pressing, or by means of a centrifugal machine. In order to separate phenol from its homologues advantage may also be taken of the property it possesses of forming a crystalline hydrate with water. In preparing pure phenol, it is necessary to repeat the solution in alkali and fractional precipitation before proceeding to rectify the oil.

Phenol crystallizes in long colourless needles, which melt at about 39° (102°·2 F.); it boils at 182° (359°·6 F.), and at 46° (114°·8 F.) has the specific gravity 1·056. It possesses a peculiar characteristic not unpleasant odour. It is moderately soluble in water, and forms with it a hydrate, $2C_6H_6O,OH_2$, which crystallizes in large six-sided prisms; it is extremely soluble in alcohol, ether, acetic acid, carbon disulphide, chloroform and hydrocarbons of the benzene series. The aqueous solution of phenol does not redden litmus; it coagulates albumen, and on this account, apparently, it is a most valuable antiseptic, preventing fermentation and putrefaction, and therefore preserving animal substances from decomposition. Phenol itself is a powerful caustic, and when applied to the skin at once whitens it; many of the haloid derivatives of phenol exhibit this property to a more pronounced extent.

Phenol is an extremely stable body, and undergoes very little decomposition when passed through a tube heated to bright redness. When fused with an excess of potassic hydrate until the mass assumes the consistence of a thick syrup, abundance of hydrogen is evolved, and although diphenol, $C_{12}H_8(OH)_2$, together with salicylic and oxybenzoic acids and other substances of unknown composition are produced, at least half the phenol employed remains unaltered, 12—15 per cent. being obtained in the form of diphenol, but the amount of acids produced does not exceed 1 per cent. of the phenol decomposed (Barth, *Ann. Chem. Pharm.*, clvi. 93).

By careful oxidation with chromic acid, phenol is converted into *phenoquinone*, $C_{18}H_{14}O_4$ (Wichelhaus, *Deut. chem. Ges. Ber.*, v. 248; 846). The oxidation probably takes place in the manner already pointed out (p. 472), hydroquinone being first produced, and converted into phenoquinone by the conjoint action of phenol and the oxidizing agent; thus:

$$\underset{\text{Hydroquinone.}}{C_6H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.} + \underset{\text{Phenol.}}{\begin{array}{l}HO.C_6H_5\\HO.C_6H_5\end{array}} + 2(O+OH_2) = \underset{\text{Phenoquinone.}}{C_6H_4\left\{\begin{array}{l}O.OC_6H_5\\O.OC_6H_5\end{array}\right.} + 4OH_2.$$

(1467) *Nitro-derivatives of Phenol.*—Nitric acid acts very violently upon phenol, but by employing acids of various degrees of concentration a series of nitrophenols may be obtained. The first product is a mixture of *paranitrophenol* with the isomeric *orthonitrophenol*, $C_6H_4(NO_2).OH$; on further nitration paranitrophenol is converted into *a*- or *paraorthodinitrophenol*, $C_6H_3(NO_2)_2.OH$, orthonitrophenol yielding the same compound, together with the isomeric β- or *diorthodinitrophenol*. Both of these dinitrophenols furnish the same *trinitrophenol* or picric acid, $C_6H_2(NO_2)_3.OH$, on treatment with nitric acid. A *metanitrophenol* is produced from the metamidonitrobenzene formed by the partial reduction of metadinitrobenzene (p. 324) by a series of reactions similar to those by which the phenols are prepared from the amido-derivatives of the hydrocarbons of the benzene series (p. 470); nitric acid converts it into a mixture of two isomeric dinitrophenols, which are not identical with those obtained from ortho- and paranitrophenol; on further nitration these furnish a trinitrophenol isomeric with that directly produced from phenol

(Bantlin, *Deut. chem. Ges. Ber.*, viii. 21). Higher nitro-derivatives of phenol are not known.

The nitrophenols are all crystalline substances more or less yellow in colour, slightly soluble in cold water, and not soluble to any great extent in boiling water; they are all readily soluble in alcohol and ether. Their properties are summarized in the following table:

Name.	Formula.	Constitution, the OH group being in the pos. 1.	Appearance.	M.P. ° C.
Paranitrophenol	$C_6H_4(NO_2)OH$	1 : 4	White prisms; non-volatile	114°
Metanitrophenol	„	1 : 3	Almost colourless prisms; non-volatile.	96°
Orthonitrophenol	„	1 : 2	Pale yellow prisms; very volatile.	45°
α- or Paraorthodinitrophenol	$C_6H_3(NO_2)_2OH$	1 : 2 : 4	Striated yellowish-white plates united in fern-like forms.	114°
β- or Diorthodinitrophenol .	„	1 : 2 : 6	Slender short pale yellow needles.	64°
γ- Dinitrophenol	„	1 : 3 : (?) 6	Slender short pale yellow needles; volatile.	104°
δ- Dinitrophenol	„	1 : 3 : (?) 4	Long slender glistening needles; non-volatile.	141°
Trinitrophenol . . . . . (from phenol)	$C_6H_2(NO_2)_3OH$	1 : 2 : 4 : 6	Pale yellow laminæ . . .	120°
Trinitrophenol . . . . . (from metanitrophenol)	„	(?) 1 : 3 : 4 : 6	Pale yellow transparent prims.	174°

The nitrophenols readily enter into reaction with metallic carbonates, and furnish a series of magnificently crystalline metallic derivatives, all more or less soluble in water; many of these derivatives are of great beauty. They vary in colour from pale yellow to brilliant crimson. The nitrophenols and their metallic derivatives all deflagrate more or less violently when ignited; many of them, especially the more highly nitrated ones, such as trinitrophenol and its derivatives, explode with considerable violence.

(1468) *Nitrosophenol:* $C_6H_4(NO).OH$.—This compound is the product of the action of nitrous acid on phenol, but its preparation requires great care. It crystallizes in large brown rhombic plates, moderately soluble in water; it melts when heated, and at 120°—130° (248°—266° F.) decomposes with a slight explosion. It is readily soluble in a dilute solution of sodic hydrate, and on the addition of a concentrated solution of the alkali sodium nitrosophenol, $C_6H_4(NO).ONa$, separates in reddish-brown needles. By reduction with tin and hydrochloric acid it is converted into paramidophenol, $C_6H_4(NH_2).OH$. On oxidation by nitric acid, or by an alkaline solution of potassic ferricyanide, it is very readily converted into paranitrophenol.

(1469) *Amido- and Amidonitro-derivatives of Phenol.*—The nitrophenols are readily converted by the action of reducing agents, such as tin and hydrochloric acid, into the corresponding amidophenols. At present only the amidophenols derived from para- and orthonitrophenol, $C_6H_4(NH_2).OH$, α-dinitrophenol, $C_6H_3(NH_2)_2.OH$, and the trinitrophenol produced from phenol, $C_6H_2(NH_2)_3.OH$, have been prepared. They are colourless crystalline bodies, but on account of the readiness with which they undergo oxidation it is difficult to prepare them in a pure state. They form well-crystallized salts with various acids; thus paramidophenol combines with hydrochloric acid, forming the hydrochloride, $C_6H_4(NH_3Cl).OH$, which crystallizes in long colourless needles; similarly, diamidophenol furnishes the hydrochloride $C_6H_3(NH_3Cl)_2.OH$, and triamidophenol the hydrochloride $C_6H_2(NH_3Cl)_3.OH$.

By the employment of less energetic reducing agents, such as ammonic sulphydrate, the higher nitrophenols may be partially reduced and converted into amidonitrophenols. At present only the compounds $C_6H_3(NO_2)(NH_2).OH$ from α-dinitrophenol and $C_6H_2(NO_2)_2(NH_2).OH$ and $C_6H_2(NO_2)(NH_2)_2.OH$ from trinitrophenol have been prepared. By the employment of an alcoholic solution of ammonic sulphydrate, amidodinitrophenol or picramic acid alone is formed, whilst with an aqueous solution, although the same compound is first produced, it is converted, by the further action of the aqueous sulphydrate, into diamidonitrophenol. These compounds crystallize in deep yellow or reddish-brown crystals; they exhibit both basic and acid properties, combining with acids to form salts such as $C_6H_2(NO_2)_2(NH_3Cl).OH$, and furnishing metallic derivatives, such as $C_6H_2(NO_2)(NH_2)_2.OAg$. Both amidodinitro- and diamidonitrophenol, however, are only monacid bases, that is to say, they combine with only a single molecule of a monobasic acid; but diamidonitrophenol has far stronger basic properties than amidodinitrophenol, being soluble even in very dilute solutions of the mineral acids and forming stable salts, whilst amidodinitrophenol dissolves only in concentrated acids, and is again precipitated on the addition of water. On the other hand, the metallic derivatives of diamidonitrophenol are far less stable than those of amidodinitrophenol, and undergo oxidation when exposed to the air in a moist state.

When amidonitrophenol is warmed with ethylic nitrite, the NH_2 group is displaced by hydrogen and *paranitrophenol* is produced, thus proving that in the formation of the amido-derivative from paraorthodinitrophenol the NO_2 group, which occupies the ortho-position, is reduced. Similarly, amidodinitrophenol is converted into α-dinitrophenol by treatment with ethylic nitrite, proving that in the reduction of trinitrophenol one of the NO_2 groups in the ortho-position is converted into the NH_2 group; although it has not been directly proved, it is probable that the nitro-group in diamidonitrophenol is in the para-position, and that in its formation from trinitrophenol the two NO_2 groups in the ortho-position undergo reduction.

(1470) *Sulphonic Acids derived from Phenol.*—Phenol readily dissolves in concentrated sulphuric acid, a considerable amount of heat being developed. The product is a mixture of the isomeric *phenolortho-* and *phenolparasulphonic acid,* $C_6H_4(OH).SO_3H$. When the phenol and acid are slowly mixed, and the mixture prevented from becoming hot, the product chiefly consists of the former, but much phenol remains unattacked. By heating for some time to about 100° (212° F.) the conversion into sulpho-acids may be rendered almost perfect, even when little more than the theoretical quantity of acid is employed, but the orthosulpho-acid then in great part undergoes conversion into the isomeric para-acid, although, apparently, however long the heating be continued, the product always contains a small amount of the phenolorthosulphonic acid.

Phenolmetasulphonic acid cannot be directly produced from phenol, but it is obtained by displacing the NH_2 group in metamidobenzenesulphonic acid by OH by Griess's method (p. 471), and as potassic salt by fusing potassic benzenemetadisulphonate with potassic hydrate (Barth and Senhofer, *Deut. chem. Ges. Ber.*, ix. 969):

$$\underset{\text{Potassic benzenemetadisulphonate.}}{C_6H_4(SO_3K)_2} + KHO = \underset{\text{Potassic phenolmetasulphonate.}}{C_6H_4(OH).SO_3K} + K_2SO_3.$$

By digesting phenol with a considerable excess of a mixture of ordinary and Nordhausen sulphuric acid at about 100° (212° F.) it is converted into *phenoldisulphonic acid*, $C_6H_3(OH)(SO_3H)_2$. Lastly, by heating phenol with a mixture of concentrated sulphuric acid and phosphoric anhydride in sealed tubes to about 180° (356° F.), a *phenoltrisulphonic acid*, $C_6H_2(OH)(SO_3H)_3$, is produced.

By heating these sulpho-acids or their salts with hydrochloric or dilute sulphuric acid in closed vessels, they are all completely decomposed with more or less readiness, phenol being reproduced, thus:

$$C_6H_4(OH).SO_3K + OH_2 = C_6H_5.OH + KHSO_4.$$

The sulpho-acids derived from the homologues of phenol and the haloid sulpho-acids of the phenols behave similarly. The decomposition takes place at temperatures varying from 100°—200° (212°—392° F.), according to the nature of the compound and the strength of the acid employed; concentrated hydrochloric acid is to be preferred. The salts of the phenolsulphonic acids usually crystallize well, and are therefore readily purified, and the isomeric and homologous sulpho-salts may, in most cases, be separated without any great difficulty by fractional crystallization, whereas the homologous and isomeric phenols and haloid phenol derivatives are usually extremely difficult to separate. This reaction therefore is of considerable practical value, as it often affords a means of separating isomeric and homologous phenols or their derivatives, and of obtaining them in a pure state; the mixed product being converted into sulpho-acids, the salts of the sulpho-acids separated by appropriate means, and then decomposed by heating with hydrochloric acid.

(1471) *Haloid Derivatives of Phenol.*—Chlorine and bromine act very readily upon phenol, much heat being developed; iodophenols are obtained by the action of iodine on phenol in presence of mercuric oxide or iodic acid. Haloid derivatives of phenol may also be prepared by Griess's method from the haloid amidoderivatives of benzene in the same manner that phenol itself is produced from amidobenzene or aniline.

Chlorophenols.—The first product of the action of chlorine on phenol is a mixture of *para-* and *orthochlorophenol*, $C_6H_4Cl.OH$, which may be separated by repeated fractional distillation; the isomeric *metachlorophenol* has not been directly produced from phenol, but it may be obtained from metachloramidobenzene or metachloraniline. Parachlorophenol is converted into *paraorthodichlorophenol*, $C_6H_3Cl_2.OH$, by the action of chlorine, and the same dichlorophenol, together with the isomeric *diorthochlorophenol*, is furnished by orthochlorophenol. Both these dichlorophenols yield the same *diorthoparatrichlorophenol*, $C_6H_2Cl_3.OH$, on further chlorination.

The conversion of phenol into trichlorophenol is effected by merely passing chlorine into the phenol, which towards the close of the operation is heated on the water bath. Under ordinary conditions, such as these may be considered, it is not possible to displace more than three atoms of hydrogen in phenol by chlorine, but when chlorine is passed into a mixture of phenol and antimonious chloride, which is heated at first on the water bath, and afterwards in a salt bath, until hydrochloric acid is no longer evolved, *pentachlorophenol*, $C_6Cl_5.OH$, is produced. Tetrachlorophenol has not been obtained. The properties of the chlorophenols are summarized in the following table:

Name.	Formula.	Constitution.	Appearance.	M.P. °C.	B.P. °C.
Parachlorophenol	$C_6H_4Cl.OH$	1 : 4	Colourless needles .	41°	218°
Metachlorophenol	„	1 : 3	Colourless oil . . .	—	214°
Orthochlorophenol	„	1 : 2	Colourless needles. .	7°	177°
Paraorthodichlorophenol. .	$C_6H_3Cl_2.OH$	1 : 2 : 4	Six-sided needles . .	43°	209°
Diorthodichlorophenol . .	„	1 : 2 : 6	Colourless needles. .	65°	219°
Paradiorthotrichlorophenol.	$C_6H_2Cl_3.OH$	1 : 2 : 4 : 6	White woolly needles	68°	244°
Pentachlorophenol . . .	$C_6Cl_5.OH$	—	Colourless needles. .	186°	—

With the exception of pentachlorophenol, which is odourless when cold, but has an intensely sharp odour and causes coughing when heated, the chlorophenols all possess an extremely unpleasant and persistent odour. Like phenol, they furnish metallic derivatives, and the mono-, di- and trichlorophenols even appear to possess more pronounced acid properties than phenol itself. They are almost insoluble in water, but readily soluble in ether and other menstrua. They are very stable compounds, being reduced but slowly by nascent hydrogen when treated with sodium amalgam and water; they are decomposed by heating with fused potassic hydrate, but the immediate products are not obtained, excepting from the monochlorophenols, which furnish the corresponding dioxybenzenes, owing to their decomposition by the potassic hydrate.

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Bromophenols.—These compounds exhibit the closest resemblance to the chlorophenols, but are less stable substances. By the first action of bromine on phenol a mixture of *para-* and *orthobromophenol* is produced, and under certain conditions not yet defined *metabromophenol* also appears to be formed. The further action of bromine on para- and orthobromophenol is similar to that of chlorine on the corresponding chlorophenols, and ceases under ordinary conditions with the production of *tribromophenol;* metabromophenol, however, is directly convertible, without heating to an elevated temperature, into tetrabromophenol. By heating tribromophenol with bromine to 170°—180° (338°—356° F.) it is converted into *tetrabromophenol,* and on further heating with excess of bromine to 210°—220° (410°—428° F.) *penta*bromophenol is produced. The following table exhibits the properties of the various bromophenols with which we are acquainted:

Name.	Formula.	Constitution.	Appearance.	M.P. °C.	B.P. °C.
Parabromophenol	$C_6H_4Br.OH$	1 : 4	Large monoclinic prisms	66°	236°
Metabromophenol	„	1 : 3	Colourless oil	...	228°
Orthobromophenol . . .	„	1 : 2	„ „ . . .	...	—
Paraorthodibromophenol .	$C_6H_3Br_2.OH$	1 : 2 : 4	Colourless prisms . . .	40°	—
Paradiorthotribromophenol	$C_6H_2Br_3.OH$	1 : 2 : 4 : 6	White silky needles . .	92°	—
Tetrabromophenol	$C_6HBr_4.OH$	...	Colourless needles . .	120°	—
Pentabromophenol	$C_6Br_5.OH$	...	„ „ . .	225°	—

Iodophenols.—The nature of the moniodophenols formed from phenol by the action of iodine in presence of mercuric oxide or iodic acid is not yet satisfactorily determined, but apparently the three isomeric moniodophenols are simultaneously produced. Pure *paraiodophenol* may be obtained by Griess's method from paramidophenol, and *orthiodophenol* is prepared in a similar manner from orthamidophenol; *metiodophenol* is obtained by displacing the NH_2 group in metiodaniline from metadinitrobenzene by OH. They are white crystalline substances, possessing a feeble, unpleasant, and most persistent odour. The only other iodophenols known are a *di-* and a *triiodophenol,* which crystallize in white needles. The melting points of these compounds are given in the following table :

Name.	Formula.	Constitution.	M.P. °C.
Paraiodophenol	$C_6H_4I.OH$	1 : 4	65°
Metiodophenol	”	1 : 3	89°
Orthiodophenol	”	1 : 2	43°
Diiodophenol	$C_6H_3I_2.OH$	(?) 1 : 2 : 4	150°
Triiodophenol	$C_6H_2I_3.OH$	(?) 1 : 2 : 4 : 6	156°

(1472) *Haloid Nitro-derivatives of Phenol.*—The monohaloid derivatives of phenol readily furnish mono- and dinitro-derivatives on treatment with nitric acid, and the dihaloid derivatives are converted by nitric acid into mono-nitro-compounds; but corresponding nitro-derivatives cannot be obtained from the trihaloid derivatives of phenol, trichlorophenol being converted into dichloroquinone, $C_6H_2Cl_2O_2$, by the action of nitric acid, whilst tribromophenol furnishes a *paranitrodibromophenol*, $C_6H_2Br_2(NO_2).OH$, one of the bromine atoms being displaced by the NO_2 group. On the other hand, the nitrophenols readily enter into reaction with the halogens, producing mono- and di-haloid nitro-derivatives, whilst the dinitrophenols furnish monohaloid derivatives; trinitrophenol, however, is converted into chlor-α-dinitrophenol by the action of chlorine in presence of iodine, and into brom-α-dinitrophenol by the action of bromine, one of the NO_2 groups in the ortho-position being displaced by the halogen.

Two isomeric mononitro-derivatives are simultaneously produced by nitrating the ortho-monohaloid derivatives of phenol, both of which furnish the same dinitro-monohaloid phenol on further nitration. Thus, orthochlorophenol is converted by nitric acid into a mixture of orthochloroparanitrophenol and orthochlororthonitrophenol, both of which on further treatment furnish orthochlororthoparadinitrophenol. Similarly, two isomeric mononitro-monohaloid derivatives are simultaneously formed by the action of halogens on orthonitrophenol, and these both furnish the same dihaloid-nitrophenol. The para-haloid derivatives and paranitrophenol do not yield isomeric compounds; the behaviour of metanitrophenol and of the meta-monohaloid derivatives of phenol has not been studied, but there is little doubt that, like the ortho-derivatives, they will furnish mixtures of isomerides.

Haloid-nitro-derivatives of phenol are also produced by the action of alkalies on certain of the haloid-nitro- and haloid-nitro-amido-derivatives of benzene; thus, the two isomeric dinitroparadichlorobenzenes furnish the sodic salts of corresponding dinitroparachlorophenols when digested with sodic hydrate solution, and bromodinitroaniline, $C_6H_2Br(NO_2)_2.NH_2$ ($NH_2 : Br : NO_2 : NO_2 = 1 : 2 : 4 : 6$), is converted into the potassic salt of bromo-α-dinitrophenol by heating with potassic hydrate solution.

The haloid-nitro-derivatives of phenol are all crystalline bodies of various shades of yellow in colour. They exhibit pronounced acid properties, and furnish a most beautiful series of well-crystallized salts, varying in colour from yellow to brilliant crimson, and more or less soluble in water. The metallic derivatives of the nitrohaloidphenols derived from paranitrophenol and α-dinitrophenol are yellow or orange; those derived from orthonitrophenol and β-dinitrophenol are mostly deep orange or red. The bromo-derivatives are mostly of a deeper colour than the corresponding chloro-derivatives, and the iodo-derivatives of a deeper colour than the corresponding bromo-derivatives. The meta-derivatives have been too little studied to enable us to state in general terms what their properties are.

The following table includes all the haloid-nitrophenols at present known:

Name.	Formula.	Constitution.	Colour of Potassium Derivative.	M.P. °C.
Orthochloroparanitrophenol	$C_6H_3Cl(NO_2)OH$	1 : 2 : 4	Yellow	111°
Orthochlororthonitrophenol	,,	1 : 2 : 6	Red	70°
Parachlororthonitrophenol	,,	1 : 4 : 2	Red	87°
Diorthochloroparanitrophenol	$C_6H_2Cl_2(NO_2)OH$	1 : 2 : 6 : 4	Orange	125°
Orthoparadichlororthonitrophenol	,,	1 : 2 : 4 : 6	Red	121°
Parachlorodiorthonitrophenol	$C_6H_2Cl(NO_2)_2OH$	1 : 4 : 2 : 6	Red	81°
Orthochloroparaorthodinitrophenol	,,	1 : 2 : 4 : 6	Yellow	111°
Metachloroparaorthodinitrophenol	,,	1 : 3 : (4 : 6 ?)	Yellow	?
Parachlororthometadinitrophenol	,,	1 : 4 : (6 : 3 ?)	Red	70°
Orthobromoparanitrophenol	$C_6H_3Br(NO_2)OH$	1 : 2 : 4	Yellow	102°
Parabromorthonitrophenol	,,	1 : 4 : 2	Red	87°
Diorthobromoparanitrophenol	$C_6H_2Br_2(NO_2)OH$	1 : 2 . 6 : 4	Orange	141°
Orthoparadibromorthonitrophenol	,,	1 : 2 : 4 : 6	Red	118°
Parabromodiorthonitrophenol	$C_6H_2Br(NO_2)_2OH$	1 : 4 : 2 : 6	Crimson	76°
Orthobromoparaorthodinitrophenol	,,	1 : 2 : 4 : 6	Orange	118°
Metabromoparaorthodinitrophenol	,,	1 : 3 : (4 : 6 ?)	Yellow	91°·5
Orthiodoparanitrophenol	$C_6H_3I(NO_2)OH$	1 : 2 : 4	Orange	94°
Pariodorthonitrophenol	,,	1 : 4 : 2	Red	(?) 110°
Diorthiodoparanitrophenol	$C_6H_2I_2(NO_2)OH$	1 : 2 : 6 : 4	Orange	156°
Orthoparadiiodorthonitrophenol	,,	1 : 2 : 4 : 6	Crimson	98°
Pariododiorthonitrophenol	$C_6H_2I(NO_2)_2OH$	1 : 4 : 2 : 6	Crimson	113°
Orthiodoparaorthodinitrophenol	,,	1 : 2 : 4 : 6	Orange	107°

(1473) *Haloid-sulpho-, Nitro-sulpho-, Amido-sulpho-,* and *Haloid-nitro-sulpho-derivatives of Phenol.*—The monohaloid derivatives of phenol readily enter into reaction with sulphuric acid forming monosulphonic acids, and by heating with an excess of the acid they are converted into disulphonic acids. Similarly, the dihaloid derivatives of phenol are converted into monosulphonic acids by the action of sulphuric acid; but the trihaloid derivatives of phenol do not furnish corresponding sulphonic acids.

Haloid phenolsulphonic acids may also be produced by the action of the halogens on the phenolsulphonic acids. Thus, on the addition of bromine to a solution of potassic phenoldisulphonate, $C_6H_3(SO_3K)_2.OH$, potassic bromophenoldisulphonate, $C_6H_2Br(SO_3K)_2.OH$, is formed, and in a similar manner potassic phenolparasulphonate, $C_6H_4(SO_3K).OH$, may be converted in succession into the *bromo*phenolparasulphonate, $C_6H_3Br(SO_3K).OH$, and the *dibromo*phenolparasulphonate, $C_6H_2Br_2(SO_3K).OH$.

It is not possible, however, to displace more than three atoms of hydrogen in phenol by the halogens and the sulpho-group, and by the continued action of the halogens in presence of water on the haloid-sulphonic acids in which substitution has taken place to this extent, the sulpho-groups are more or less readily displaced by the halogen. For example, on adding bromine to a solution of potassic bromophenoldisulphonate it is converted into the dibromomonosulphonate, and by the continued action of bromine on the latter tribromophenol is produced:

$$\underset{\text{Potassic bromophenoldisulphonate.}}{C_6H_2Br(SO_3K)_2.OH} + Br_2 + OH_2 = \underset{\text{Potassic dibromophenolsulphonate.}}{C_6H_2Br_2(SO_3K).OH} + HBr + HKSO_4.$$

$$\underset{\text{Potassic dibromophenolsulphonate.}}{C_6H_2Br_2(SO_3K).OH} + Br_2 + OH_2 = \underset{\text{Tribromophenol.}}{C_6H_2Br_3.OH} + HBr + HKSO_4.$$

The phenolsulphonic acids behave similarly with nitric acid. Thus, potassic phenolparasulphonate is converted by careful nitration into potassic orthonitro-phenolparasulphonate, $C_6H_3(NO_2)(SO_3K).OH$. Orthonitrophenolparasulphonic acid is also produced by gently warming orthonitrophenol with sulphuric acid, and the isomeric paranitrophenolorthosulphonic acid is obtained in a similar manner from paranitrophenol; by careful nitration these acids may be converted into dinitrophenolsuphonic acids, which by the continued action of nitric acid are converted into trinitrophenol. Sulpho-acids have not been directly produced from the dinitrophenols.

The nitrophenolsulphonic acids are converted by the action of reducing agents into corresponding amidophenolsulphonic acids, which may also be produced from the amidophenol hydrochlorides by treatment with sulphuric acid.

Apparently, the haloid-nitro-phenols do not enter into reaction with sulphuric acid to produce corresponding sulpho-acids, but on treatment with nitric acid the monohaloid-phenolmonosulphonic acids furnish mononitro-monohaloid-phenolsulphonic acids, and similar compounds are formed from the monohaloid-disulpho-acids, one of the sulpho-groups being displaced by NO_2; by the further action of nitric acid these haloid-nitro-sulpho-acids are converted into haloid-dinitrophenols. The dihaloid-phenolmonosulphonic acids are either converted into dihaloid-nitrophenols by the action of nitric acid, or one of the atoms of halogen is displaced by NO_2, and haloid-nitro-sulpho-acids are produced.

The phenolsulphonic acids and their derivatives furnish two classes of salts: *normal salts*, formed by the displacement of hydrogen in the sulpho-group by metals, and so-called *basic salts*, in which not only the hydrogen in the sulpho-group, but also that in the OH group, is displaced by metals. The salts of the phenol- and haloid-phenolsulphonic acids are colourless; the normal salts of the nitrophenol- and haloid-nitrophenolsulphonic acids are yellow, but the basic salts of these acids vary in colour from yellow to red, and many of them are of great beauty. Apparently, there is a similar connexion between colour and constitution as in the case of the nitrophenols, the basic salts of orthonitrophenol derivatives being usually of a more or less red colour.

Formula.	Constitution.*	Source.
1. $C_6H_4.OH.SO_3H$	1 : 2	From phenol and sulphuric acid.
2. $C_6H_4.OH.SO_3H$	1 : 4	„ „
3. $C_6H_3.OH.(SO_3H)_2$	1 : 2 : 4	From 1 and 2 by action of sulphuric acid.
4. $C_6H_3Cl.OH.SO_3H$	1 : 2 : 4	From parachlorophenol.
5. $C_6H_3Cl.OH.SO_3H$	1 : 4 : 2	From orthochlorophenol.
6. $C_6H_2Cl_2.OH.SO_3H$	1 : 4 : 2 : 6	From 2 by action of chlorine.
7. $C_6H_2Cl_2.OH.SO_3H$	1 : 2 : 4 : 6	From orthoparadichlorophenol.
8. $C_6H_2Cl.OH.(SO_3H)_2$	1 : 2 : 4 : 6	From 3 by action of chlorine.
9. $C_6H_2Cl.OH.(SO_3H)_2$	1 : 2 : 6 : 4	From parachlorophenol and H_2SO_4.
10. $C_6H_3Br.OH.SO_3H$	1 : 2 : 4	From 1 and bromine, and from parabromophenol.
11. $C_6H_3Br.OH.SO_3H$	1 : 4 : 2	From 2 and bromine.
12. $C_6H_2Br_2.OH.SO_3H$	1 : 4 : 2 : 6	From 2 and bromine.
13. $C_6H_2Br_2.OH.SO_3H$	1 : 2 : 4 : 6	From 1 and bromine, and from 14 and bromine.
14. $C_6H_2Br.OH.(SO_3H)_2$	1 : 2 : 4 : 6	From 3 and bromine.
15. $C_6H_2I_2.OH.SO_3H$	1 : 4 : 2 : 6	From 2 by action of iodine in presence of HgO.
16. $C_6H_3(NO_2).OH.SO_3H$	1 : 2 : 4	From paranitrophenol and H_2SO_4.
17. $C_6H_3(NO_2).OH.SO_3H$	1 : 4 : 2	From orthonitrophenol and H_2SO_4, and from 2 and HNO_3.
18. $C_6H_3(NH_2).OH.SO_3H$	1 : 2 : 4	From 16 by reduction, and from paramidophenol.
19. $C_6H_3(NH_2).OH.SO_3H$	1 : 4 : 2	From 17 by reduction, and from orthamidophenol.
20. $C_6H_2Cl(NO_2).OH.SO_3H$	1 : 2 : 4 : 6	From 4 and HNO_3.
21. $C_6H_2Cl(NO_2).OH.SO_3H$	1 : 4 : 2 : 6	From 6 and HNO_3.
22. $C_6H_2Br(NO_2).OH.SO_3H$	1 : 4 : 2 : 6	From 12 and HNO_3, and from 17 and bromine.
23. $C_6H_2Br(NO_2).OH.SO_3H$	1 : 2 : 6 : 4	From 16 and bromine.
24. $C_6H_2Br(NO_2).OH.SO_3H$	1 : 2 : 4 : 6	From 10 and nitric acid.
25. $C_6H_2I(NO_2).OH.SO_3H$	1 : 2 : 6 : 4	From 16 by action of iodine in presence of HgO.
26. $C_6H_2I(NO_2).OH.SO_3H$	1 : 4 : 6 : 2	From 17 by action of iodine „ „ HgO.

* The OH group is always supposed to occupy the position 1; the relative position of the sulpho-group is next stated, then that of the halogen, and lastly that of the nitro-group.

The foregoing table includes all the phenolsulphonic acids and substituted phenolsulphonic acids of known constitution which have been prepared from phenol and phenol derivatives.

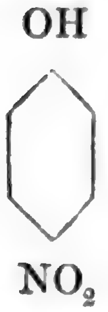
(1474) *Mode of Determining the Constitution of Phenol Derivatives.*—Much discussion has taken place of late with regard to the constitution of the phenol derivatives, but the conclusions at which chemists have now arrived are so consistent that there can scarcely be a doubt as to their correctness. After the explanation we have given of the manner in which the constitution of the benzene derivatives is determined, it will only be necessary briefly to indicate the method adopted in the case of the phenol derivatives.

We may conveniently commence with the three nitrophenols, since most phenol derivatives can be more or less directly referred to these compounds. Their connexion with the three isomeric dibromobenzenes is established in the following manner. By heating the two isomeric nitrobromobenzenes produced by the action of nitric acid on bromobenzene with potassic hydrate solution, the potassium derivatives of the two nitrophenols which are formed on nitrating phenol are obtained:

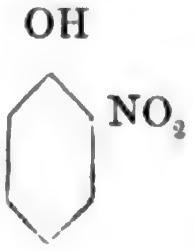
$$\underset{\text{Bromonitrobenzene.}}{C_6H_4Br.NO_2} + 2KHO = \underset{\text{Potassium nitrophenol.}}{C_6H_4(NO_2).OK} + KBr + OH_2;$$

but these two nitrobromobenzenes are respectively convertible into *para-* and *ortho*dibromobenzene: that which furnishes the non-volatile modification of nitrophenol yielding paradibromobenzene. Hence it follows that the non-volatile nitrophenol (M.P. 114° C.) formed on nitrating phenol is *paranitrophenol* ($OH : NO_2 = 1 : 4$), whilst the isomeric volatile modification (M.P. 45° C.) is *orthonitrophenol* ($OH : NO_2 = 1 : 2$). The third isomeride is consequently *metanitrophenol*, ($OH : NO_2 = 1 : 3$), and this is confirmed by its production from the modification of dinitrobenzene which is convertible into metadibromobenzene. These conclusions are supported by many other conversions which need not be detailed here; in fact, no reactions are known which are not in accordance with them.

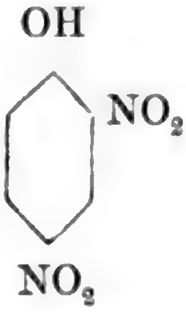
The constitution of the mononitrophenols being known, that of α-dinitrophenol is readily inferred from its formation from both ortho- *and* paranitrophenol, whilst the fact that both α- and β-dinitrophenol furnish metadinitrobenzene ($NO_2 : NO_2 = 1 : 3$) when the OH group is displaced by hydrogen, proves that in the β-compound both NO_2 groups occupy ortho-positions. The constitution of trinitrophenol (from phenol) is deduced in a similar manner from the observation that it may be produced by the nitration of both *a- and* β-dinitrophenol. The following symbols, however, will render more evident the nature of the relation to each other of the various nitrophenols formed on nitrating phenol:



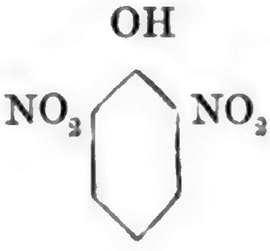
Paranitrophenol.
M.P. 114°



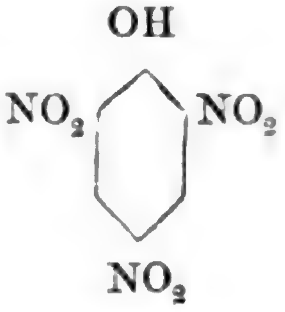
Orthonitrophenol.
M.P. 45°



a-Dinitrophenol.

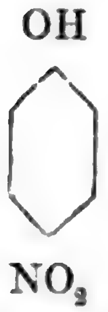


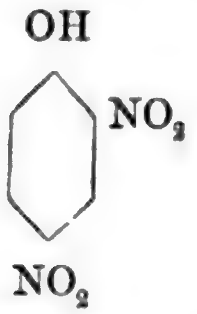
β-Dinitrophenol.

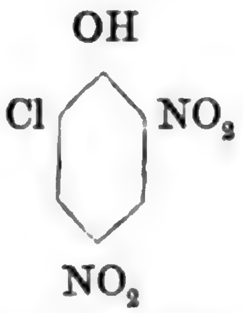


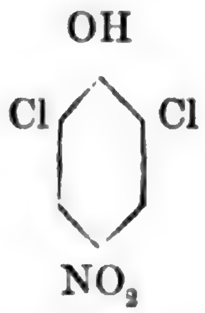
Trinitrophenol.

By displacing the NO_2 group in paranitrophenol by chlorine, by Griess's method, it is converted into the chlorophenol (B.P. 218° C.) which is the main product of the action of chlorine on phenol; the isomeric chlorophenol (B.P. 176° C.) from phenol may in a similar manner be obtained from orthonitrophenol. From this it follows that the two chlorophenols produced on chlorinating phenol are respectively para- and orthochlorophenol. The constitution of the monochlorophenols has also been established by their formation from the three isomeric chloramidobenzenes or chloranilines, and by their conversion into dichlorobenzenes by the action of phosphoric pentachloride. On chlorination both para- and orthochlorophenol furnish the dichlorophenol (M.P. 43° C.) which is the main product of the continued action of chlorine on phenol, thus proving it to be paraorthochlorophenol. The constitution of the isomeric dichlorophenol (M.P. 65° C.) which is formed in small quantity on chlorinating phenol is deduced in not quite so direct a manner. It may be obtained by displacing the NO_2 group in dichloro*para*nitrophenol by hydrogen, but by the action of nitric acid on the latter compound *orthochloro-a-dinitrophenol* is produced, one of the atoms of chlorine being displaced by NO_2; since, however, *a*-dinitrophenol is an orthopara-derivative of phenol, it follows that the chlorine atom which is displaced occupies the ortho-position, and that consequently both chlorine atoms in dichloroparanitrophenol occupy ortho-positions as an *ortho*chlorodinitrophenol is formed by treating it with nitric acid. Thus:

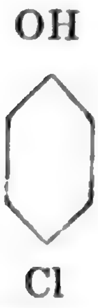

Paranitrophenol.

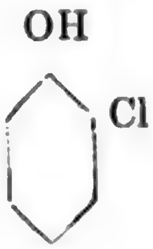

α-Dinitrophenol.

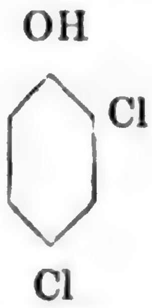

Orthochlor-α-dinitrophenol.

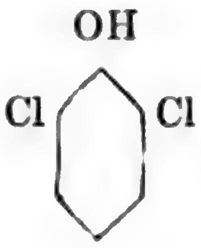

Dichloroparanitrophenol.

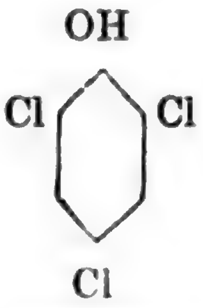
Lastly, since both the above-mentioned dichlorophenols furnish the same trichlorophenol when chlorinated, this compound must be a diorthochloroparachloro-derivative. We may, therefore, represent the series of chlorophenols formed on chlorinating phenol by the following symbols, which it will be noticed exactly correspond to those assigned to the nitrophenols :


Parachlorophenol.
B.P. 176°

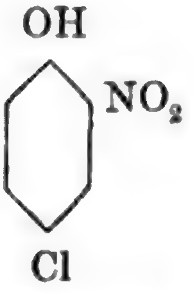

Orthochlorophenol.
B.P. 218°


Dichlorophenol.
M.P. 43°

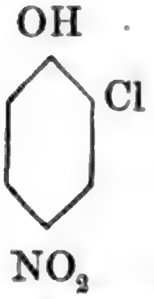

Dichlorophenol.
M.P. 65°


Trichlorophenol.

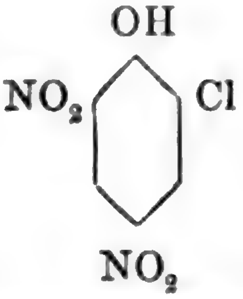
The constitution of the bromo- and iodophenols may be deduced in a similar manner, and that of the haloid nitrophenols is also readily ascertained since they have been obtained, on the one hand, by nitrating haloid phenols of known constitution, and on the other, by the action of the halogens on nitrophenols of known constitution. For example, a single chloronitrophenol is obtained on nitrating *parachloro*phenol which is identical with one that is formed on chlorinating *orthonitro*phenol; it is, therefore, parachlororthonitrophenol. *Paranitro*phenol, when chlorinated, furnishes an isomeric paranitrochlorophenol, which may also be obtained by nitrating *orthochloro*phenol, and is, therefore, paranitroorthochlorophenol. A third nitrochlorophenol is obtainable by nitrating orthochlorophenol, and as on further nitration it yields orthochloro-α-dinitrophenol, which may also be formed by nitrating orthochloroparanitrophenol, it must of necessity be an *ortho*chlor*ortho*nitrophenol; thus:



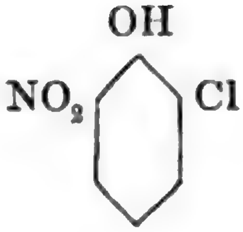
Parachlororthonitrophenol.



Orthochloroparanitrophenol.



Orthochlor-α-dinitrophenol.



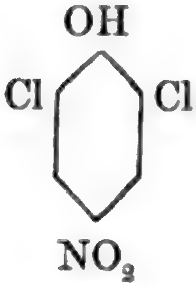
Orthochlororthonitrophenol.

The fact that the phenol*meta*sulphonic acid produced by displacing one of the sulpho-groups in benzenemetadisulphonic acid by OH (p. 479) is not identical with either of the phenolsulphonic acids formed by the action of sulphuric acid on phenol necessitates the conclusion that the compounds directly produced from phenol are the *ortho-* and *para-* acid. By its conversion into parachlorophenol by distillation with phosphoric pentachloride, the stable modification is shown to be the para-acid:

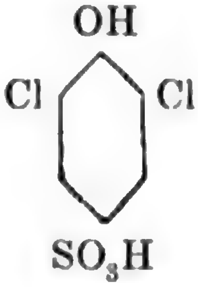
$$C_6H_4(SO_3H).OH + 2PCl_5 = C_6H_4Cl.OH + SOCl_2 + 2POCl_3 + HCl;$$

whilst the connexion of the unstable modification with the ortho-series, which follows from this observation, is confirmed by its conversion into orthodioxybenzene or pyrocatechin, $C_6H_4(OH)_2$, on fusion with potassic hydrate.*

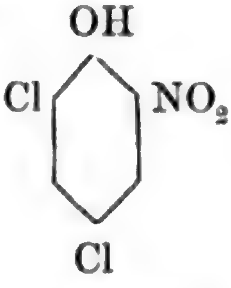
The dichlorophenolsulphonic acid obtained by chlorinating the stable phenolsulphonic acid from phenol is converted into dichloro*para*nitrophenol by the action of nitric acid, whilst that produced from the unstable modification furnishes dichlor*ortho*nitrophenol. If, from a consideration of the evidence above given, we regard the constitution of the phenolsulphonic acids from phenol as established, these results may be regarded as a proof that when the phenolsulphonic acids are converted into corresponding nitro-derivatives by the action of nitric acid, the SO_3H or sulpho-group is directly displaced by the NO_2 group; thus:



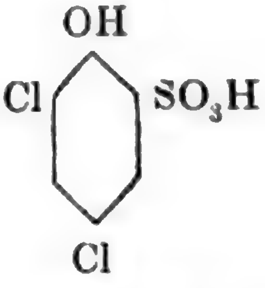
Dichloroparanitrophenol.



Dichlorophenolparasulphonic acid.



Dichlororthonitrophenol.



Dichlorophenolorthosulphonic acid.

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* Although isomeric change not unfrequently takes place when such compounds as the sulphonic acids are fused with potassic hydrate, the formation of the ortho-modification of dioxybenzene has never been observed in any case in which the production of its isomerides is to be expected (see Dioxybenzenes).

It will now be understood without further explanation that the constitution of the haloid- and haloid-nitro-phenolsulphonic acids is readily inferred from their formation from the haloid-phenols, &c., and from their conversion into haloid-nitrophenols of known constitution.

(1475) *The Law of Substitution in the Phenol Series.*—On comparing together the various compounds produced *directly* from phenol, it will be evident that the formation of substitution derivatives from it is regulated by very simple laws, which, briefly stated, are as follows:

1. That the action of the halogens, and of nitric and sulphuric acids, and probably of reagents generally, on phenol is similar, inasmuch as the same hydrogen atoms are always displaced.

2. That under what may be termed ordinary conditions at most three atoms of hydrogen in phenol may be displaced. Thus, the action of nitric acid ceases with the production of trinitrophenol, which, however, is formed without difficulty. Similarly, chlorine, bromine, and iodine readily convert phenol into the corresponding trihaloid derivatives, but higher derivatives are only obtained on heating to a comparatively high temperature, or by the aid of powerful agents such as antimony pentachloride.

3. That the three atoms of hydrogen which may be displaced are those which occupy the ortho-positions, 1 : 2 and 1 : 6, and the para-position, 1 : 4; *meta-* or 1 : 3 and 1 : 5 derivatives being rarely produced. Thus, neither nitric nor sulphuric acid appears to have any tendency to form meta-derivatives, neither have they been obtained by the action of chlorine, whilst metabromophenol is produced apparently only under special conditions. At present it is not known whether metiodophenol is a constant product of the action of iodine on phenol, but it probably is.

4. That a mixture of the ortho- and para-mono-derivatives, in proportions which vary according to the conditions of experiment, is always produced in the first instance: the exact manner in which the proportions vary with the conditions has not been ascertained. On further treatment, the para-mono-derivatives always furnish paraortho-di-derivatives, but the ortho-mono-derivatives yield paraortho-di-derivatives and a variable amount of the diortho-di-derivatives; both the paraortho- and the diortho-di-derivatives are finally converted into para-diortho-tri-derivatives.

The meta-mono-derivatives of phenol apparently resemble phenol itself in their behaviour, metabromophenol being readily converted into tetrabromophenol by the action of bromine. It is also probable that the order in which substitution is effected is the same, since the two dinitrophenols formed on nitrating metanitrophenol exhibit considerable resemblance to the two nitrophenols obtained from phenol: the one being non-volatile and soluble in water, and the other volatile, thus agreeing in properties with para- and orthonitrophenol respectively, and we may therefore infer that they are similarly constituted.

(1476) ALCOHOLS OF THE COMPOSITION $C_7H_7.OH = 108$.—Four alcohols derived from toluene are known—viz., benzylic alcohol, $C_6H_5.CH_2(OH)$, and the three isomeric cresols, $CH_3.C_6H_4.OH$.

(1477) *Benzylic Alcohol* or *Phenylcarbinol*: $C_6H_5.CH_2(OH)$.—According to Kraut, Peru balsam consists essentially of benzylic cinnamate, $C_7H_7O.C_9H_7O$, from which benzylic alcohol may be obtained by treating it with potassic hydrate; benzylic ethers are also present in Tolu balsam and liquid storax. To prepare the alcohol from toluene, $C_6H_5.CH_3$, the heated hydrocarbon is submitted to the action of chlorine; the benzylic chloride, $C_6H_5.CH_2Cl$, thus produced is converted into the acetate by heating it with potassic acetate, and the acetate saponified with potassic hydrate; or the chloride may be directly converted into the alcohol by heating it with plumbic hydrate and water. Benzylic alcohol is also produced together with potassic benzoate by the action of an alcoholic solution of potassic hydrate on benzoic aldehyde, $C_6H_5.COH$, and together with hydrobenzoin and other substances when benzoic acid is treated with sodium amalgam.

It is a colourless, highly refractive, oily liquid, insoluble in water, possessing a feeble pleasant odour; it boils at 207° (404°·6 F.), and at 0° (32° F.) has the specific gravity 1·06. It remains liquid at −18° (−0°·4 F.). On oxidation, it furnishes benzoic aldehyde and benzoic acid. When distilled with a concentrated potassic hydrate solution a portion is converted into potassic benzoate, and another portion reduced to toluene.

The chlorinated toluenes of the formula $C_6H_{5-n}Cl_n.CH_2Cl$ yield chlorinated derivatives of benzylic alcohol when converted into the corresponding acetates, and these are subsequently saponified; these substances, of which the complete series has been obtained, are colourless crystalline bodies (Beilstein and Kuhlberg).

Mononitrobenzylic alcohol, $C_6H_4(NO_2).CH_2(OH)$, prepared from metanitrobenzoic aldehyde by treatment with alcoholic solution of potassic hydrate, is a viscid oil (Grimaux, *Ann. Chem. Pharm.*, cxlv. 47), whilst the compound obtained by saponifying nitrobenzylic acetate (formed by dropping benzylic acetate into fuming nitric acid) crystallizes in slender colourless needles, which melt at 93° (199°·4 F.). As it yields paranitrobenzoic acid on oxidation, it is evidently a para-derivative. By the action of fuming nitric acid it is converted into dinitrobenzylic alcohol; this crystallizes in needles which melt at 71° (159°·8 F.) (Beilstein and Kuhlberg, *ibid.*, cxlvii. 339).

(1478) *Cresol* or *Methylphenol*: $CH_3.C_6H_4.OH$.—Para- and orthocresol are obtained respectively from the potassic salts of the para- and orthotoluenesulphonic acids produced on warming toluene with sulphuric acid by fusing them with potassic hydrate. They may also be prepared from the corresponding nitrotoluenes. Metacresol is prepared by heating thymol or methylpropylphenol with phosphoric anhydride, when propylene is evolved, and a cresylic phosphate produced from which metacresol is obtained by fusion with potassic hydrate; it is also formed on distilling the baric salt of oxyuvitic acid, $C_6H_2(OH)(CH_3)(COOH)_2$, with lime or baryta (Oppenheim and Pfaff, *Deut. chem. Ges. Ber.*, viii. 886). Orthocresol is prepared in a similar manner from carvacrol, the isomeride of thymol. Coal tar oil certainly contains both para- and orthocresol, and probably also metacresol.

Paracresol is a white crystalline substance which melts at 36° (96°·8 F.); according to Schiff (*ibid.*, viii. 1201), it boils at 198°—199° (388°·4—390°·2 F.). Metacresol has only been obtained as a liquid, boiling at 200°—201° (392°—393°·8 F.). Orthocresol is a crystalline solid which melts at 31° (87°·8 F.), and boils at 185°—186° (365°—366°·8 F.) (Kekulé, *ibid.*, vii. 1007). When oxidized by fusion with potassic hydrate, paracresol is converted into paroxybenzoic acid, and metacresol into the isomeric metoxybenzoic acid, orthocresol yielding salicylic or orthoxybenzoic acid: the third acid of the composition $C_6H_4(OH)COOH$. By the action of a mixture of potassic chlorate and hydrochloric acid, which exercises simultaneously a chlorinating and an oxidizing action, metacresol is converted into a dichlorotoluquinone, $C_7H_4Cl_2O_2$, orthocresol yielding a mixture of a di- and trichlorotoluquinone, but paracresol does not furnish a quinone derivative.

Very little is known of the derivatives of the cresols. On nitration, paracresol is converted into an orthonitroparacresol, melting at 33° (91°·4 F.), which in all respects is the analogue of orthonitrophenol; on further nitration this yields a diorthonitroparacresol, melting at 84° (183°·2 F.), which very closely resembles diorthonitrophenol. Paracresol, however, cannot be converted into a trinitro-derivative, but metacresol yields without difficulty a trinitrometacresol, resembling trinitrophenol, and which melts at about 105° (221° F.). Similarly, by the action of bromine on the sulpho-acid produced by dissolving paracresol in sulphuric acid, a bromoparacresolorthosulphonic acid is produced, but a higher brominated derivative of this acid cannot be obtained, the sulpho-group being displaced by bromine by the further action of the latter.

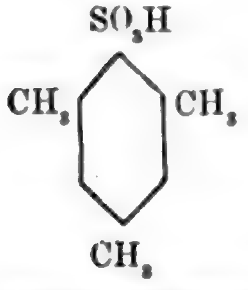
(1479) ALCOHOLS OF THE COMPOSITION $C_8H_9.OH = 122$.—No less than eight of these alcohols have been described, but none of them have been sufficiently investigated.

Paratolylic Alcohol or *Tolylcarbinol:* $CH_3.C_6H_4.CH_2(OH)$ (CH_3:$CH_2(OH)$ = 1 : 4), is produced on heating paratoluic aldehyde with an alcoholic solution of potassic hydrate (Cannizzaro, *Compt. Rend.*, liv. 1225). It is a white crystalline substance, which melts at 59° (138°·2 F.), and boils at 217° (422°·6 F.); it is reconverted into the aldehyde, $CH_3.C_6H_4.COH$, by oxidation.

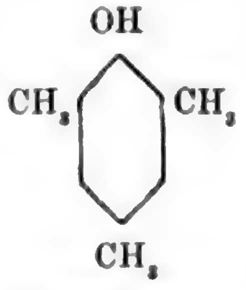
Secondary Phenylethylic Alcohol or *Methylphenylcarbinol:* $CH_3.CH(C_6H_5).OH$, is obtained by the action of nascent hydrogen on methylphenylketone, $CH_3.CO.C_6H_5$, and by saponifying the acetate formed from bromethylbenzene, $C_6H_5.CHBr.CH_3$, and argentic acetate with sodic hydrate solution (Radziszewsky, *ibid.*, vii. 140). It is a colourless highly refractive liquid of unpleasant odour, which boils at about 203° (397°·4 F.); on oxidation it is reconverted into the ketone.

Primary Phenylethylic Alcohol: $C_6H_5.CH_2.CH_2(OH)$, is obtained by the action of sodium amalgam on an aqueous alcoholic solution of phenylacetic aldehyde, $C_6H_5.CH_2.COH$. It is a colourless liquid of faint odour, of the specific gravity 1·0337 at 21° (69°·8 F.), and boils at 212° (413°·6 F.). It furnishes phenylacetic aldehyde and phenylacetic acid on oxidation. *Primary phenylethylic acetate*, $C_6H_5.CH_2.CH_2.C_2H_3O_2$, is a colourless liquid, possessing a powerful, pleasant odour, which boils without decomposition at 224° (435°·2 F.); it readily furnishes the alcohol on saponification with potassic hydrate (Radziszewsky, *Deut. chem. Ges. Ber.*, ix. 372). When it is added to an excess of acetic chloride, chiefly acetic acid and chlorethylbenzene, $C_6H_5.CHCl.CH_3$, are produced. *Secondary phenylethylic acetate* has a pleasant jasmine-like odour, and boils at 213°—216° (415°·4—420°·8 F.), but is at the same time partially decomposed into acetic acid and cinnamene. It cannot be saponified with an alcoholic solution of potassic hydrate: the chief products in this case being cinnamene and metacinnamene.

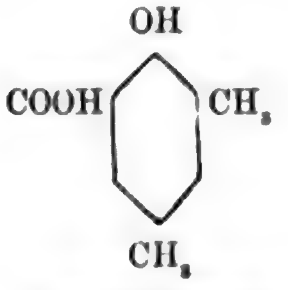
Xenol, Xylenol or *Oxydimethylbenzene:* $C_6H_3(CH_3)_2.OH$.—When coal-tar xylene, consisting chiefly of metadimethylbenzene, is converted into sulpho-acid, and the potassic salt of the latter is fused with potassic hydrate, a mixture of phenols is produced, from which a crystalline metaxenol, $C_6H_3(CH_3)_2.OH$, and a liquid isomeric phenol, which is probably paraxenol derived from the paradimethylbenzene present in coal-tar xylene, may be separated. The crystalline xenol is also formed on fusing mesitylenesulphonic acid with potassic hydrate; in this case not only is the sulpho-group displaced by OH, but one of the methyl groups is oxidized to COOH, and the elements of a molecule of carbonic anhydride are also removed. This latter method of formation, it will be evident, enables us to infer the constitution of the crystalline xenol; thus:



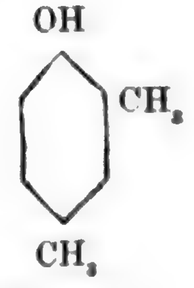
Mesitylenesulphonic acid.



Oxymesitylene.



Oxymesitylenic acid.



Metaxenol.

But on *à priori* grounds it is probable that the xenol from metaxylene has the constitution assigned to it, independently of the evidence afforded by its formation from mesitylene, as it has been observed that when di-derivatives of benzene are converted into tri-derivatives the tendency is always to form a 1 : 2 : 4 derivative, so that the conversion of metadimethylbenzene ($CH_3 : CH_3 = 1 : 3$) into the sulpho-acid ($HSO_3 : CH_3 : CH_3 = 1 : 2 : 4$) is what is to be expected.

Metaxenol crystallizes in large colourless prisms, which are very volatile, and melt at 75° (167° F.); it boils at about 215° (419° F.). It is scarcely soluble in water, but dissolves in all proportions in alcohol and ether. When dissolved in glacial acetic acid and mixed with bromine, it is converted into dibromometaxenol, which crystallizes in white needles, melting at about 81° (177°·8 F.); the same compound is obtained on adding bromine to a solution of the metaxenolsulphonic acid produced by the action of sulphuric acid on metaxenol. When, however, bromine is added to metaxenol suspended in water and the product is crystallized from alcohol, a substance which crystallizes in golden yellow plates, melting at about 180° (356° F.), is obtained, the nature of which has not yet been satisfactorily ascertained; it would appear to be a dibromo-derivative of a compound containing proportionally less hydrogen than the xenol from which it is derived.

Liquid xenol has a somewhat lower boiling point than the crystalline isomeride, but has not yet been examined.

Ethylphenol or *Oxyethylbenzene:* $C_2H_5.C_6H_4.OH$.—Ethylbenzene, like methylbenzene or toluene, when heated with concentrated sulphuric acid, furnishes a mixture of two isomeric sulpho-acids, and from the general resemblance in behaviour between methyl- and ethylbenzene it can scarcely be doubted that the two acids are respectively *para-* and *ortho*ethylbenzenesulphonic acid. On heating the potassic salts of the crude product with potassic hydrate, a mixture of the corresponding ethylphenols is produced. From this mixture the chief product may be separated by fractional distillation and cooling the distillate; it is then obtained in large colourless transparent prismatic crystals, which melt at about 47° (116°·6 F.). It boils at 209°—210° (408°·2—410° F.), according to Fittig and Kiesow; at 214°—215° (417°·2—419° F.), according to Beilstein and Kuhlberg. Unlike metaxenol, it instantly liquefies in contact with water, but like the former it is very volatile. The isomeric ethylphenol has not yet been separated in a pure state; it is said to be a liquid boiling at 212° (413°·6 F.). No derivatives of either of these phenols have as yet been prepared.

Phlorol is obtained by distilling the baric salt of phloretic acid, $C_9H_{10}O_3$, with lime. It is a colourless liquid, resembling phenol in odour, but does not solidify when cooled to − 18° (− 0°·4 F.); it boils at about 220° (428° F.). It is said to be converted into a trinitro-derivative by concentrated nitric acid.

Phloretic acid yields *para*oxybenzoic acid when fused with potassic hydrate, and methylphloretic acid is converted into paramethoxybenzoic or anisic acid, $C_6H_4(OCH_3).COOH$, on oxidation. Hence it would seem that there are but two side-chains in phloretic acid, and since the one is hydroxyl, the conclusion is forced upon us that it is a *phenolpropionic* acid, $C_6H_4(OH).C_2H_4.COOH$, in which the OH and $C_2H_4.COOH$ groups relatively occupy the positions 1 and 4. But if this be the constitution of phloretic acid, it follows that phlorol must be *paraethylphenol:*

$$C_6H_4(OH).C_2H_4.COOH = C_6H_4(OH).C_2H_5 + CO_2.$$

It does not seem, however, to be identical with the crystalline ethylphenol from ethylbenzene, which there is every reason to believe is paraethylphenol; moreover, judging from the behaviour of paracresol, it is improbable that paraethylphenol would furnish a trinito-derivative. From this it will be seen that at present the constitution of phlorol is uncertain. According to Marasse (*Ann. Chem. Pharm.*, clii. 75), a colourless, oily liquid, isomeric or identical with the above, is contained in beech-tar, and is found in that portion of the phenols which distils between 217° and 220° (422°·6—428° F.). The oil extracted from the roots of *Arnica montana*, according to Sigel, contains phlorol as isobutyric ether (*ibid.*, clxx. 345).

(1480) ALCOHOLS OF THE COMPOSITION C_9H_{11}.OH = 136.—Only three monohydric alcohols derived from hydrocarbons of the composition C_9H_{12} are known.

Primary Phenylpropylic Alcohol: $C_6H_5.CH_2.CH_2.CH_2(OH)$, is present in storax, probably as a cinnamic ether, and is contained in commercial cinnamic alcohol. It may be prepared by the action of nascent hydrogen on cinnamic alcohol, C_9H_{19}.OH. It is a colourless, thick liquid, of the specific gravity 1·008 at 18° (64°·4 F.), which boils at 235° (455° F.); on oxidation it yields hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$ (Fittig, *Deut. chem. Ges. Ber.*, vi. 215).

Secondary Phenylpropylic Alcohol: $C_2H_5.CH(C_6H_5).OH$, is produced from ethylphenyl ketone, $C_2H_5.CO.C_6H_5$, by the action of nascent hydrogen. It boils at about 210° (410° F.), but is partially decomposed (Barry, *ibid.*, vi. 1008).

Mesitol or *Oxymesitylene:* $C_6H_2(CH_3)_3$.OH.—This phenol is produced by carefully fusing the potassic salt of mesitylenesulphonic acid with potassic hydrate, and from nitromesitylene by displacing the NO_2 group by OH (p. 471). It crystallizes in long white needles, which melt at 68°—69° (154°·4—156°·2 F.); bromine converts it into a monobromo-derivative, which melts at 80° (176° F.) (Biedermann and Ledoux, *Deut. chem. Ges. Ber.*, viii. 57—250).

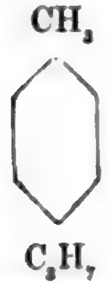
(1481) ALCOHOLS OF THE COMPOSITION $C_{10}H_{13}$.OH = 150.—*Cumic* or *Cuminylic Alcohol:* $C_3H_7.C_6H_4.CH_2(OH)$, produced from cumic aldehyde, is a colourless liquid, of faint but agreeable aromatic odour, which boils at 243° (469°·4 F.); on oxidation it yields cumic acid, $C_3H_7.C_6H_4.COOH$, which by further oxidation may be converted into terephthalic acid, $C_6H_4(COOH)_2$, proving that the C_3H_7 and $CH_2(OH)$ groups in the alcohol are relatively in the para-position. By the action of an alcoholic solution of potassic hydrate it is converted into cymene and potassic cuminate (Kraut, *Ann. Chem. Pharm.*, xcii. 66).

Phenylpropylcarbinol: $C_3H_7.CH(C_6H_5)$.OH, has been prepared from the corresponding ketone, but not yet examined.

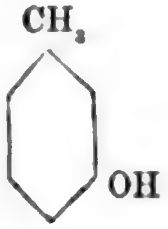
Thymol: $C_3H_7^{\alpha}.C_6H_3(CH_3)$.OH.—This phenol is contained together with terpenes and cymene in various essential oils, such as oil of thyme, the oil of *Ptychotis Ajowan* and the oil of *Monarda punctata*. It crystallizes in large colourless prisms, possessing an agreeable odour of thyme, which melt at 44° (111°·2 F.); it boils at 230° (446° F.). On oxidation with sulphuric acid and manganese dioxide it furnishes thymoquinone, $C_{10}H_{12}O_2$. A number of substitution derivatives of thymol have been prepared, but little is known of their properties. It is stated that by the prolonged action of chlorine it is converted into *pentachlorothymol*, and that *pentabromothymol* is produced by the action of bromine in sunlight; when bromine is added to a solution of the thymolsulphonic acid formed by dissolving thymol in sulphuric acid, a bromothymolsulphonic acid is produced, which is converted by the further action of bromine into *dibromothymol*, which separates as an oil. Similarly, by treating the sulpho-acid with nitric acid, a crystalline *dinitrothymol* is readily produced, and it is stated this may be converted into *trinitrothymol* by dissolving it in a mixture of concentrated nitric and sulphuric acids (Lallemand, *Ann. Chem. Pharm.*, ci. 119, cii. 119). When thymol is distilled with phosphoric pentachloride the OH group is displaced by chlorine, and from the chlorocymene thus produced cymene may be obtained by the action of nascent hydrogen.

Carvacrol: $C_3H_7^{\alpha}.C_6H_3(CH_3)$.OH, the isomeride of thymol may be obtained from the sulpho-acid prepared from cymene or paramethylpropylbenzene by fusing it with potassic hydrate, and by heating camphor with one-third of its weight of iodine; it is also produced when carvol, a neutral body of the same composition as carvacrol, which is a constituent of oil of caraway, is warmed with a small quantity of orthophosphoric acid, the carvol then undergoing isomeric change. Carvacrol is an oily liquid which boils at about 233° (451°·4 F.). Its derivatives have not yet been examined. On oxidation, it is converted into thymoquinone identical with that produced from thymol.

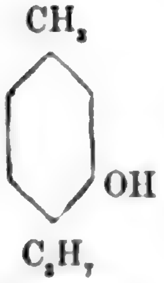
The cymene obtained from thymol is identical with that from which carvacrol may be prepared; hence it follows that thymol and carvacrol are both derivatives of the same paramethylpropylbenzene or cymene, and this conclusion is confirmed by the observation that both furnish thymoquinone on oxidation. The position of the OH group may readily be deduced from the fact that thymol is converted into *meta*cresol, and carvacrol into *ortho*cresol, by the action of phosphoric anhydride: it will be evident on comparing the following symbols that in thymol the OH group is in the meta-position relatively to the methyl-group, whilst in carvacrol it occupies the ortho-position:



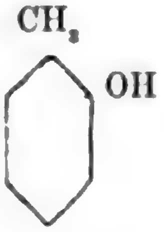
Cymene.



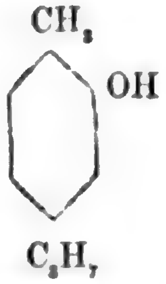
Metacresol.



Thymol.



Orthocresol.



Carvacrol.

(1482) *Sycocerylic Alcohol:* $C_{18}H_{29}.OH$.—This alcohol is produced by treating sycocerylic acetate, a constituent of the resin of *Ficus rubiginosa* from New South Wales, with sodic ethylate. It forms very slender crystals, which melt at 90° (194° F.), and distils partly undecomposed. Little is known of the properties of this body (De la Rue and Miller, *Jour. Chem. Soc.*, v. 62).

In concluding this brief account of the alcohols derived from the hydrocarbons of the benzene series, we may refer the student to Watts' "Dictionary of Chemistry," vol. iv. and 1st and 2nd supplement, for further particulars as to their preparation and properties.

§ V. MONOHYDRIC ALCOHOLS DERIVED FROM HYDROCARBONS ISOLOGOUS WITH BENZENE.

(1483) *Alcohols derived from the Hydrocarbons of the* C_nH_{2n-8} *or Cinnamene Series.*—Only four are known—viz., *cinnamic alcohol* and the phenol *anol,* both of which have the composition $C_9H_{10}O$, and the isomeric bodies, *cholesterin* and *isocholesterin,* $C_{26}H_{44}O$.

Cinnamic Alcohol: $C_6H_5.CH{=\!=}CH.CH_2(OH)$, is obtained on distilling cinnamic cinnamate or styracin (a constituent of liquid storax and of Peru balsam), $C_9H_7O_2.C_9H_9$, with a concentrated solution of potassic hydrate.

It crystallizes in colourless glistening needles possessing a pleasant odour, sparingly soluble in water, but readily soluble in alcohol; it melts at 33° (91°·4 F.), and boils at 250° (482° F.). When carefully oxidized, it furnishes cinnamic acid, $C_9H_8O_2$. It combines directly with bromine, forming the compound $C_6H_5.CHBr.CHBr.CH_2(OH)$; on treatment with hydrochloric acid gas, it furnishes chlorocinnamene, $C_6H_5.CH{=}CH.CH_2Cl$; by the action of nascent hydrogen it is in part converted into allylbenzene, and in part into phenylpropylic alcohol.

Anol or *Allylphenol:* $C_3H_5.C_6H_4.OH$, is prepared by carefully heating anethol, $C_3H_5.C_6H_4.OCH_3$, with fused potassic hydrate; the product is dissolved in water, and on adding an acid the anol is precipitated in yellow flocculi. In thus precipitating it from the alkaline solution it is necessary to keep the liquid cold, or it separates as a black oil, which soon resinifies.

Anol crystallizes from hot water in white glistening plates, which melt at 92°·5 (198°·5 F.); it boils at about 250° (482° F.). It dissolves in alcohol, ether, and chloroform: it does not always crystallize from these solutions, but sometimes, especially when the solution is exposed to the air, it passes into the condition of a brown liquid insoluble in water.

Cholesterin: $C_{26}H_{43}.OH$, is a substance which occurs very frequently both as an animal and a vegetable product. It is present in various parts of the animal system; in biliary calculi, of which it sometimes constitutes nearly the entire substance; in the yolk of egg; in the fat extracted from the fleece of sheep, chiefly in the form of ethereal salts of acids of the acetic and oleic series; and in various vegetable substances, in the fixed oils, for example, and seeds such as peas, wheat, and maize.

Cholesterin is tasteless, inodorous, insoluble in water, and sparingly soluble in cold alcohol, but easily soluble in boiling alcohol; it crystallizes with a molecule of water in thin white shining plates, which melt at about 144° (291°·2 F.). Its solutions exert a lævorotatory action on polarized light. On adding sodium to a solution of cholesterin in petroleum, sodic cholesterylate, $C_{26}H_{43}.ONa$, is formed with evolution of hydrogen. By the action of phosphoric pentachloride, or by heating with concentrated hydrochloric acid, the OH group in cholesterin may be displaced by chlorine. Cholesterylic chloride, $C_{26}H_{43}Cl$, is a crystalline substance, which melts at 100° (212° F.); when digested with ammonia, it furnishes cholesterylamine, $C_{26}H_{43}.H_2N$, which crystallizes in colourless plates melting at 104° (219°·2 F.). Cholesterin also enters into reaction with acids, forming ethereal salts: thus, by heating it with benzoic acid at 200° (392° F.), it is converted into cholesterylic benzoate, $C_{26}H_{43}O.C_7H_5O$, which crystallizes from ether in small glistening plates, melting at 150° (302° F.) (Schulze, *Journ. pr. Chem.* [2], vii. 163); the acetate, $C_{26}H_{43}O.C_2H_3O$, formed by the action of acetic chloride, crystallizes in small colourless needles, which melt at 92° (197°·6 F.) (Loebisch, *Deut. chem. Ges. Ber.*, v. 510). Cholesterin combines with a molecule of bromine, forming the compound $C_{26}H_{43}Br_2.OH$; this crystallizes in small colourless needles, melting at 147° (296°·6 F.), and is reconverted into cholesterin by the action of nascent hydrogen (Wislicenus and Moldenhauer, *Ann. Chem. Pharm.*, cxlvi. 175). By oxidation with potassic dichromate and sulphuric acid, cholesterin is converted into a white amorphous acid, having the composition of oxycholic acid, $C_{26}H_{40}O_6$, small quantities of acids of the acetic series being also produced (Loebisch; compare Latschinoff, *Deut. chem. Ges. Ber.*, ix. 1311).

Isocholesterin accompanies cholesterin in wool-grease (Schulze, *loc. cit.*). It separates from a dilute alcoholic solution in white flocculi, but a hot concentrated solution solidifies on cooling to a transparent jelly; it crystallizes from ether and acetone in fine transparent needles, which melt at 137°—138° (278°·6—280°·4 F.). Isocholesterylic benzoate separates from ether as a crystalline powder, which under the microscope is seen to consist of fine needles; it melts at 190° (374° F.). Phosphoric pentachloride converts it into the chloride $C_{26}H_{43}Cl$. If cholesterin is dissolved in a small quantity of chloroform and the solution shaken with an equal volume of concentrated sulphuric acid, the chloroform quickly becomes blood-red and then cherry-red or purple, but isocholesterin does not exhibit this behaviour.

(1484) ALCOHOLS DERIVED FROM NAPHTHALENE. *Naphthols.*—When the SO_3H group in the two isomeric sulphonic acids produced by the action of sulphuric acid on naphthalene is displaced by OH, in the usual manner, by fusing their potassic salts with potassic hydrate, &c., two isomeric alcohols, *α- and β-naphthol*, $C_{10}H_7.OH$, are obtained, which bear precisely the same relation to naphthalene that phenol bears to benzene, and which closely resemble phenol in properties; these naphthols may also be prepared from *α*- and *β*-amidonaphthalene, or naphthylamine, $C_{10}H_7.H_2N$, by Griess's method (Schaeffer, *Ann. Chem. Pharm.*, clii. 279; Maikopar, *Zeits. Chem.* [2], v. 215).

Both are colourless crystalline substances, easily soluble in alcohol, ether, chloroform, or benzene, but sparingly soluble in hot water and almost insoluble in cold water. *α*-Naphthol crystallizes from water in small needles, *β*-naphthol in laminæ; the crystals of the former belonging to the monoclinic, and those of the latter to the rhombic system. α-Naphthol melts at about 95° (203° F.), and boils at 278°—280° (532°·4—536° F.); it has a faint odour resembling that of phenol. β-Naphthol melts at 123° (253°·4 F.), and boils at 285°—290° (554° F.); it is almost odourless. α-Naphthol readily volatilizes with the vapour of water, but the β-compound volatilizes only to a very slight extent. The aqueous solution of α-naphthol becomes dark violet on adding bleaching powder solution, and red, passing to violet, when ferric chloride is added; the solution of β-naphthol is coloured pale yellow by bleaching powder solution, and pale green by ferric chloride. The naphthols dissolve readily in alkalies, and sodium and potassium act upon them with evolution of hydrogen; but their metallic derivatives are far less stable than those of phenol, and are decomposed when their aqueous solutions are evaporated. By the action of carbonic anhydride on their sodium derivatives, the sodic salts of oxy-acids are produced, corresponding to those obtained in a similar manner from the phenols. On warming with concentrated sulphuric acid, they are dissolved and converted into naphtholsulphonic acids, $C_{10}H_6(OH).SO_3H$.

By distilling β-naphthol with phosphoric pentachloride it is converted into β-chloronaphthalene (1368), $C_{10}H_7Cl$ (Rimarenko, *Deut. chem. Ges. Ber.*, ix. 663).*

The only haloid derivative of naphthol at present known is the *dibrom-a-naphthol*, $C_{10}H_5Br_2.OH$, which is produced on adding bromine to a solution of *a*-naphthol in acetic acid. It crystallizes in long colourless glistening needles, which melt at 111° (231°·8 F.). It is readily converted into trioxynaphthalene, $C_{10}H_5(OH)_3$, by treatment with an alcoholic solution of potassic hydrate (Biedermann, *ibid.*, vi. 1119).

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* According to Rimarenko, β-chloronaphthalene melts at 56° (132°·8 F.), and boils at 264°—266° (507°·2—510°·8 F.). Atterberg, in a recent communication (*ibid.*, ix. 926), states that the chloronaphthalene obtained from nitronaphthalene (1367) is the α-compound, and not the isomeric β-derivative as he formerly supposed.

α-Chloronaphthalene is converted by the action of cold nitric acid of sp. gr. 1·4 into a nitro-α-chloronaphthalene, which crystallizes in fine pale-yellow needles, melting at 85° (185° F.); this compound furnishes α-naphthylamine on reduction (Atterberg). When α-chloronaphthalene is treated with fuming nitric acid, a dinitro-α-chloronaphthalene melting at 180° (356° F.) is produced, together with that melting at 105° (221° F.): the quantity obtained being greater, the higher the temperature at which the nitration is effected (Atterberg). Some light has recently been thrown on the formation of isomeric chloronaphthalenes from naphthalene by the discovery that, when pure naphthalene tetrachloride (1367) is decomposed by an alcoholic solution of potassic hydrate, apparently only α-dichloronaphthalene melting at 36° (96°·8 F.) is produced; whereas, when it is decomposed by rapidly heating small quantities to boiling, chiefly the isomeric β-compound melting at 68° (154°·4 F.) is obtained, and by heating larger quantities and maintaining the liquid in the state of gentle ebullition until hydrochloric acid ceases to be evolved, a mixture of β-dichloronaphthalene with a considerable amount of the α-compound is formed (Krafft and Becker, *ibid.*, ix. 1088).

(1485) *Nitroso-*, *Nitro-*, and *Amido-derivatives* of *a*- and *β*-*Naphthol*.— When submitted to the action of nitrous acid, *a*-naphthol furnishes a mixture of two isomeric nitrosonaphthols, $C_{10}H_6(NO).OH$ (Fuchs, *ibid.*, viii. 625). *a-Nitroso-a-Naphthol* crystallizes in needles, and when precipitated from its solution in alkalies by the addition of an acid is of a pure white colour; it melts between 175° and 185° (347° and 365° F.), but undergoes decomposition. *β-Nitroso-a-Naphthol*, which is the chief product, is yellow, and melts at 145°—150° (293°—302° F.), but is also decomposed; it is easily soluble in benzene, in which the isomeride is only sparingly soluble.

The preparation of nitro-derivatives directly from the naphthols is extremely difficult, *a*-naphthol being almost entirely converted into resinous substances by the action of nitric acid; they are readily procured by indirect methods however: thus, by boiling the two isomeric nitro-derivatives produced on nitrating acet-*a*-amidonaphthalene* (pp. 349, 350) with sodic hydrate solution, they are converted into the sodium derivatives of the corresponding nitronaphthols (Biedermann and Andreoni, *ibid.*, vi. 342; Biedermann, vi. 1117; Liebermann and Dittler, vii. 240; Liebermann, viii. 680):

$$C_{10}H_6(NO_2).NH(C_2H_3O) + 2NaOH = C_{10}H_6(NO_2).ONa + NH_3 + Na\,C_2H_3O_2.$$

The two nitro-*a*-naphthols may also be obtained by carefully oxidizing the corresponding nitrosonaphthols (Fuchs), and *a*-nitro-*a*-naphthol is produced in small quantity when a mixture of 1 pt. nitronaphthalene, 1 pt. potassic hydrate, and 2 pts. slaked lime is heated to 140° (284° F.), in a retort through which a current of oxygen or air is slowly passed; the latter method, which is due to Dusart, has been employed for the preparation of nitronaphthol on the large scale, this compound being used as a yellow dye, but on account of the smallness of the yield it is no longer manufactured (Darmstaedter and Nathan, *ibid.*, iii. 943; Liebermann and Dittler, vii. 244).

a-Nitro-a-Naphthol, which is obtained from the nitro-*a*-amidonaphthalene melting at 191° (375°·8 F.), is very soluble in alcohol, from which it crystallizes in very slender lemon-yellow interlaced needles; it melts at 164° (327°·2 F.). *β-Nitro-a-Naphthol*, from the nitro-*a*-amidonaphthalene which melts at 159° (318°·2 F.), is much less soluble in alcohol, and crystallizes in isolated needles much thicker than those of its isomeride; it melts at 128° (262°·4 F.). They dissolve in alkaline solutions and decompose metallic carbonates, forming metallic derivatives which crystallize well, and are mostly of a red colour. Both α-and-β-nitro-α-naphthol furnish phthalic acid on oxidation with nitric acid, which is a proof that the NO_2 and OH group in each of them are in the same benzene nucleus.

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* The product obtained on nitrating acet-*a*-amidonaphthalene is a mixture of three isomeric bodies, two of which, however, melt at the same temperature (171° C.), but are converted by the action of alkalies into distinct nitro-*a*-amidonaphthalenes melting respectively at 191° and 159° C.; the third isomeride melts at 189° C., but also furnishes the nitro-*a*-amidonaphthalene melting at 191° C. (Liebermann and Dittler, *ibid.*, vii. 240). The nature of the isomerism between the two compounds which furnish the same nitro-amidonaphthalene is not yet explained, but it appears probable that they belong to the class of "physical isomerides."

The nitronaphthols are converted by reduction into corresponding amidonaphthols, the hydrochlorides of which may be obtained in colourless crystals; α-amido-α-naphthol readily furnishes naphthaquinone on oxidation, but this compound cannot be obtained from β-amido-α-naphthol (Liebermann and Dittler, *ibid.*, vii. 243).

Dinitro-α-naphthol, $C_{10}H_5(NO_2)_2.OH$, which is the final product of nitration that can be obtained from α-naphthol, may be produced by the action of nitric acid on the nitroso- and nitro-α-naphthols (Fuchs), or on α-naphthol-sulphonic acid (Darmstaedter and Wichelhaus, *ibid.*, ii. 113), and by displacing the NH_2 group in dinitro-α-amidonaphthalene by OH by boiling it with a solution of sodic hydrate (Liebermann and Hammerschlag, *ibid.*, ix. 333). It may also be prepared by adding potassic nitrite to a solution of α-naphthylamine hydrochloride, and subsequently heating the solution with nitric acid (Martius); the naphthylamine salt is thus converted into diazonaphthalene hydrochloride, which is decomposed on warming with water, and the naphthol produced is at once converted into the dinitro-compound by the nitric acid present. It crystallizes in sulphur-yellow needles, which melt at 138° (280°·4 F.); its metallic derivatives are orange or red in colour, and the nitro-compound itself is one of the most beautiful of yellow dyes. On boiling with nitric acid it furnishes phthalic acid.

By the action of nascent hydrogen, dinitro-α-naphthol is converted into *diamido-α-naphthol*, $C_{10}H_5(NH_2)_2.OH$; the hydrochloride of this compound is converted into the hydrochloride of the so-called *diimidonaphthol* on treatment with ferric chloride, and by heating the latter with water, the so-called *oximidonaphthol* is produced, which furnishes *oxynaphthaquinone* when boiled with hydrochloric acid (Graebe and Ludwig, *Ann. Chem. Pharm.*, cliv. 303):

$$C_{10}H_5\left\{\begin{matrix}OH\\NH_2\\NH_2\end{matrix}\right. + Fe_2Cl_6 = C_{10}H_5\left\{\begin{matrix}\left.\begin{matrix}O\\NH\end{matrix}\right\}^{*}\\NH_2\end{matrix}\right. + 2FeCl_2 + 2HCl.$$

Diamidonaphthol.

$$C_{10}H_5\left\{\begin{matrix}\left.\begin{matrix}O\\NH\end{matrix}\right\}\\NH_2\end{matrix}\right. + OH_2 = C_{10}H_5\left\{\begin{matrix}\left.\begin{matrix}O\\NH\end{matrix}\right\}\\OH_2\end{matrix}\right. + NH_3.$$

$$C_{10}H_5\left\{\begin{matrix}\left.\begin{matrix}O\\NH\end{matrix}\right\}\\OH\end{matrix}\right. + OH_2 + HCl = C_{10}H_5\left\{\begin{matrix}\left.\begin{matrix}O\\O\end{matrix}\right\}\\OH\end{matrix}\right. + NH_4Cl.$$

Oxynaphthaquinone.

Dinitro-β-naphthol, the only nitro-derivative of β-naphthol at present known, is produced on treating an alcoholic solution of β-naphthol with dilute nitric acid. It crystallizes in pale yellow needles, which melt at 195° (383° F.). It furnishes a number of difficultly soluble, yellow or red metallic derivatives (Wallach and Wichelhaus, *Deut. chem. Ges. Ber.*, iii. 846).

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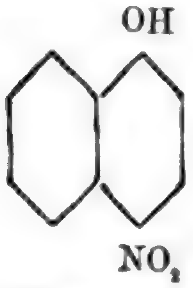
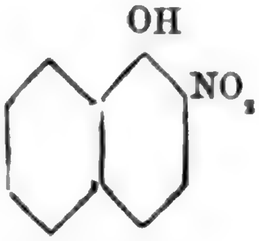
* Graebe and Ludwig assign to this compound the formula $C_{10}H_5(OH)\left\{\begin{matrix}NH\\NH\end{matrix}\right\}$, and they assume that in its formation from diamidonaphthol each of the NH_2 groups in the latter is deprived of an atom of hydrogen, and that the nitrogen

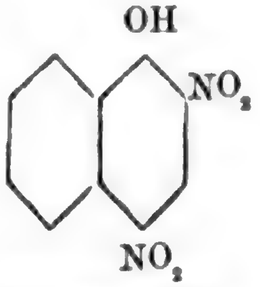
(1486) *Constitution of the Naphthol Derivatives.*—The manner in which the constitution of the naphthols themselves may be inferred has already been explained (1366). The constitution of their derivatives has not yet been experimentally demonstrated in the same rigorous manner as that of the phenol derivatives, but the close agreement in general behaviour between phenol and the naphthols, and in the properties of their derivatives, appears to warrant the conclusion that the constitution of the naphthol derivatives is similar to that of the corresponding phenol derivatives produced under similar conditions. Applying, therefore, to the naphthols, the law of substitution which obtains in the case of phenol, we may represent their nitro-derivatives in the following manner:



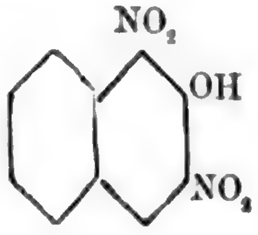
α-Nitro-α-naphthol.



β-Nitro-α-naphthol.

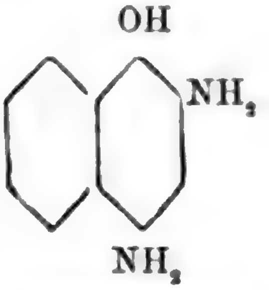


Dinitro-α-naphthol.

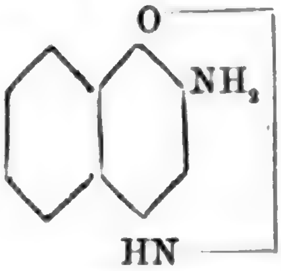


Dinitro-β-naphthol.

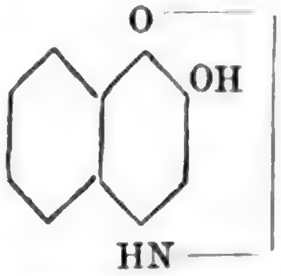
The relation which the so-called diimodonaphthol and oximidonaphthol probably bear to diamido-α-naphthol is indicated by the following formulæ:



Diamido-α-naphthol.



? Diimidonaphthol.



? Oximidonaphthol.

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atoms then become united by one affinity of each; but according to our view of the constitution of diamidonaphthol and of the quinones, it appears more probable that only one of the NH_2 groups loses an atom of hydrogen, the second being withdrawn from the OH group; if this be the case, the so-called diimodonaphthol is the amido-derivative of a compound intermediate between naphthaquinone and diimidonaphthalene:

$$C_{10}H_6\left\{\begin{matrix}O\\O\end{matrix}\right\} \quad ; \quad C_{10}H_6\left\{\begin{matrix}O\\NH\end{matrix}\right\} \quad ; \quad C_{10}H_6\left\{\begin{matrix}NH\\NH\end{matrix}\right\}.$$

Naphthaquinone. Diimidonaphthalene.

According to Heintzel (*Journ. pr. Chem.*, c. 193), triamidophenol (1469) exhibits a similar behaviour, its hydrochloride being converted on exposure to air into the hydrochloride of a compound to which Kekulé (*Lehrbuch*, iii. 66) has assigned the formula $C_6H_2(OH)\left\{\begin{matrix}NH\\NH\\NH_2\end{matrix}\right\}$, but which is more probably the diamido-derivative of an "imidoquinone," $C_6H_2(NH_2)_2\left\{\begin{matrix}O\\NH\end{matrix}\right\}$; by boiling with water it is converted into the hydrochloride of a new compound, which is perhaps formed by the displacement of one of the NH_2 groups by OH, and may therefore be represented by the formula $C_6H_2(NH_2)\left\{\begin{matrix}OH\\NH\\NH\end{matrix}\right\}$.

We may here also direct attention to the conclusion which may be drawn as to the constitution of the two isomeric dinitronaphthalenes produced on nitrating naphthalene (1370), if the formula above given is the correct expression of the constitution of dinitro-α-naphthol, and if naphthaquinone is analogous in constitution to ordinary quinone (p. 349). Thus, according to Liebermann and Hammerschlag (*Deut. chem. Ges. Ber.*, ix. 333), the dinitronaphthalene from which dinitro-α-naphthol is derived, and which may be obtained by displacing the NH_2 group in dinitro-α-amidonaphthalene by hydrogen, is not identical with either of the dinitronaphthalenes from naphthalene; moreover, the diamidonaphthalenes obtained on reducing the latter do not furnish any naphthaquinone on oxidation, whereas the diamidonaphthalene from the nitro-α-amidonaphthalene which is convertible into α-nitro-α-naphthol readily furnishes naphthaquinone on oxidation (Liebermann and Dittler, *ibid.*, vi. 949). Hence we may conclude that in neither of the two dinitronaphthalenes from naphthalene are the NO_2 groups relatively in the position 1 : 4 or 1 : 3, since that in which the NO_2 groups are in the position 1 : 4 would furnish a diamidonaphthalene yielding naphthaquinone on oxidation, whilst that in which $NO_2 : NO_2 = 1 : 3$ would be identical with the dinitronaphthalene from dinitro-α-amidonaphthalene. Therefore, in one of the two dinitronaphthalenes from naphthalene, the NO_2 groups are probably in the position 1 : 2 in the same nucleus, whilst the other is doubtless formed by the displacement of two atoms of hydrogen in different nuclei. This result is of interest, as it indicates that the displacement of hydrogen in naphthalene is not necessarily confined to the one nucleus, although this appears to be more generally the case.

(1487) ALCOHOLS DERIVED FROM HYDROCARBONS OF THE C_nH_{2n-14} SERIES.—Four monohydric alcohols derived from hydrocarbons of the diphenyl series are at present known to us, viz.:

		M.P. °C.
Paraphenylphenol	$C_6H_5.C_6H_4.OH$	165°
Benzylphenol	$C_6H_5.CH_2.C_6H_4.OH$	84°
Diphenylcarbinol	$(C_6H_5)_2CH.OH$	68°
Tolylphenylcarbinol	$C_6H_5.CH_2.C(C_6H_5)H.OH$	62°

Paraphenylphenol or *Oxydiphenyl*: $C_6H_5.C_6H_4.OH$, is obtained by displacing the SO_3H group in diphenylparasulphonic acid by OH by fusing it with potassic hydrate, &c. (Engelhardt and Latschinoff, *Deut. chem. Ges. Ber.*, vi. 194); it may also be produced from the amidodiphenyl obtained on reducing paranitrodiphenyl (Osten, *ibid.*, vii. 173). It crystallizes in minute needles, which melt at 164°—165° (327°·2—329° F.), and boils at 305—308° (581°—586°·4 F.); it is easily soluble in alcohol and solutions of caustic alkalies, and volatilizes with the vapour of water. It does not produce a coloration with ferric chloride. By the action of concentrated sulphuric acid, it is converted into a mixture of mono- and di-sulphonic acids. On nitration it furnishes a mixture of a mono- and a dinitro-derivative; the mononitro-compound, $C_6H_5.C_6H_3(NO_2).OH$, crystallizes in lemon-yellow prisms, and melts at 67° (152°·6 F.), whilst the dinitro-derivative, $C_6H_5.C_6H_2(NO_2)_2.OH$, crystallizes in golden-yellow plates, and melts at 154° (309°·2 F.); only the former volatilizes with the vapour of water. Both furnish red metallic derivatives, but those of the mono-nitro-compound are extremely unstable. Oxydiphenyl is converted into parachlorodiphenyl when distilled with phosphoric pentachloride (1374).

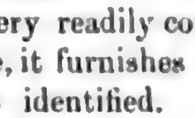
Benzylphenol: $C_6H_5.CH_2.C_6H_4.OH$, is the product of the action of benzylic chloride on phenol in presence of zinc; it is probable that the para- and ortho-modifications are formed simultaneously in this reaction, although only a single benzylphenol has been isolated. Benzylphenol crystallizes in white silky needles or lustrous plates, soluble in alcohol, ether, benzene and alkaline solutions; it melts at 84° (183°·2 F.). When heated with concentrated sulphuric acid, it is converted into a disulphonic acid, and bromine gives rise to a crystalline body, melting at about 175° (347° F.), which is probably a dibromo-derivative. By the combined action of sodium and carbonic anhydride, it is converted into the sodium salt of benzyloxybenzoic acid, $C_6H_5.CH_2.C_6H_3(OH).COOH$ (Paterno, *Journ. Chem. Soc.*, xxv. 702; xxvii. 371).

The acetate, $C_6H_5.CH_2.C_6H_4.O(C_2H_3O)$, formed by the action of acetic chloride, is a liquid which, on exposure to the air, absorbs water and becomes decomposed. The corresponding benzoate crystallizes in thin plates and glistening needles; it melts at 86° (186°·8 F.), and is not decomposed by water or an aqueous solution of potassic hydrate. The behaviour of benzylphenol on oxidation has not been investigated, but from its mode of formation it is probable that it is a para-derivative of phenol, and that it would yield paroxybenzoic acid.

Diphenylcarbinol or *Benzhydrol:* $(C_6H_5)_2CH.OH$, is formed by treating diphenylketone, $C_6H_5.CO.C_6H_5$, dissolved in dilute alcohol, with sodium amalgam. It crystallizes in slender silky needles, which melt at 68° (154°4 F.), and boils at about 298° (568°·4 F.), being partially decomposed and converted into the ether $(C_6H_5)_2CH.O.CH(C_6H_5)_2$. It is sparingly soluble in water, but dissolves more easily in alkaline liquids; on the addition of water to a concentrated solution of potassic hydrate saturated with diphenylcarbinol, the alcohol is deposited in the crystalline form. It dissolves with facility in alcohol and other menstrua. On treatment with bromine, it furnishes a crystalline dibromo-derivative, which is not affected by heating with moist argentic oxide or potassic hydrate solution, and, therefore, probably has the formula $(C_6H_4Br)_2CH.OH$. On oxidation, it is converted into diphenylketone (Linnemann, *Ann. Chem. Pharm.*, cxxxiii. 6).

Tolylphenylcarbinol or *Toluylene Hydrate:* $C_6H_5.CH_2.C(C_6H_5)H.OH$, is obtained on treating an alcoholic solution of deoxybenzoin or tolylphenylketone, $C_6H_5.CH_2.CO.C_6H_5$, with sodium amalgam; and, together with benzoic acid, by the action of an alcoholic solution of potassic hydrate on hydrobenzoin, $C_6H_5.CH(OH).CH(OH).C_6H_5$. It crystallizes in long, slender, brittle needles, insoluble in water, but very soluble in alcohol and ether; it melts at 62° (143°·6 F.), and distils without decomposition. It is very readily converted into deoxybenzoin by oxidation. On treatment with bromine, it furnishes bromotolane, $C_{14}H_9Br$, together with other substances not yet identified. When boiled with dilute sulphuric acid, it is converted into stilbene or toluylene, $C_{14}H_{12}$, and water (Limpricht and Schwanert, *ibid.*, clv. 60).

(1488) DIPHENYLENECARBINOL or *Fluorene Alcohol:*



$$\left.\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}\right\rangle CH.OH$$

the only monohydric alcohol derived from the hydrocarbons of the C_nH_{2n-16} series at present known to us, is obtained by the action of sodium amalgam on an alcoholic solution of diphenyleneketone (1383). It crystallizes in hexagonal plates, which melt at 153° (307°·4 F.); when heated for some time above its fusing point it is converted into the ether $(C_{12}H_9)_2O$. It readily furnishes diphenyleneketone on oxidation (Barbier, *Compt. Rend.*, lxxx. 1396).

(1489) ALCOHOLS DERIVED FROM ANTHRACENE. *Anthrols.*—By fusing the potassic salts of the two anthracenesulphonic acids (p. 373) with potassic hydrate, they may be converted into corresponding oxyanthracenes or anthrols, $C_{14}H_9.OH$ (Linke, *Journ. pr. Chem.* [2], xi. 227). *α-Anthrol* crystallizes in glistening pale yellow needles and plates, insoluble in water, but easily soluble in alcohol, ether and benzene; it decomposes at 250° (482° F.), without fusing. *β-Anthrol* forms yellowish prisms, less soluble in alcohol and ether than the α-compound; when heated, it also decomposes without fusing. Both dissolve in sulphuric acid, forming sulphonic-acids, and furnish bromo-derivatives when treated with bromine. They dissolve easily in alkalies, and when the solutions are heated in presence of air, coloured oxidation products separate (comp. Anthraquinone).

(1490) TRIPHENYLCARBINOL: $C(C_6H_5)_3.OH$, is formed on treating triphenylbromomethane with water, and by the action of a mixture of potassic dichromate and sulphuric acid on triphenylmethane (1402). It crystallizes from alcohol, ether, or benzene, in which it is easily soluble, in brilliant monoclinic plates, which melt at 157° (314°·6 F.); it boils without decomposition at a temperature above 360° (680° F.). It dissolves in cold concentrated sulphuric acid, but is reprecipitated on the addition of water. On treatment with bromine or nitric acid, it furnishes substitution derivatives difficult of purification; the nitro-derivative does not dissolve in alkalies. When its solution in toluene is boiled with sodium, hydrogen is evolved and an insoluble pulverulent sodium derivative produced. When submitted to the action of acetic or benzoic chlorides it is converted into the corresponding acetate or benzoate, but these compounds are decomposed even by exposure to moist air.

§ VI. DIHYDRIC ALCOHOLS OF THE $C_nH_{2n}(OH)_2$ OR GLYCOLIC SERIES. THE GLYCOLS.

(1491) The alcohols of this series are derived from the paraffins by the displacement of two atoms of hydrogen by twice the group OH, but dihydric alcohols having very different properties are obtained, according as the two atoms of hydrogen which are displaced are associated with the same or with different atoms of carbon: those in which the two OH groups are attached to different carbon atoms being tolerably stable bodies, distilling without decomposition; whilst those in which both OH groups are united with the same carbon atom are so unstable that they cannot be isolated. The alcohols of the former class are termed *glycols*; those of the latter class may be called *aldehydrols* on account of their relation to the aldehydes, from which they may be regarded as formed by the conversion of the COH group into the group $CH(OH)_2$ by the addition of the elements of a molecule of water.

As we have already pointed out, the possibility of the existence of compounds in which more than one OH group is associated with the same carbon atom is disputed by some chemists, chiefly on the ground that they cannot be isolated; and the existence of bodies of the "aldehydrol" class is explained by the assumption that they are mere molecular combinations similar to salts with water of crystallization: chloral hydrate, for example, according to this view, is a molecular combination of trichloraldehyde and water, $CCl_3.COH + OH_2$, and has not the constitution represented by the formula $CCl_3.CH(OH)_2$. We are acquainted, however, with too many instances of the decomposition of bodies by heat to attach much weight to the argument drawn from the instability of those compounds in which we may suppose two OH groups to be associated with the same carbon; atom moreover, the mere fact that a body cannot be isolated in a pure state is no proof that it cannot exist under favourable conditions. But the most important evidence that aldehydrols may exist is furnished by the behaviour of the aldehydes, and when treating of these compounds we shall have occasion to show that many of their reactions, which otherwise are difficult to account for, are at once explained in a simple and consistent manner if it be assumed that they exist in aqueous solution as "aldehydrols." The part which these bodies appear to play in the formation of aldehydes from the monohydric alcohols of the ethylic series by oxidation has already been indicated (p. 418).

(1492) *Methods of Preparing Dihydric Alcohols of the* $C_nH_{2n}(OH)_2$ *Series.*—The most general method of preparing the glycols consists in acting upon the dihaloid derivatives of the paraffins, in which the two atoms of halogen are associated with different carbon atoms, with argentic or potassic acetate, and saponifying the resulting acetates:

$$C_nH_{2n}Br_2 + 2AgC_2H_3O_2 = C_nH_{2n}(C_2H_3O_2)_2 + 2AgBr.$$

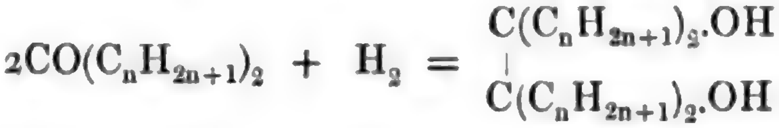
$$C_nH_{2n}(C_2H_3O_2)_2 + 2KHO = C_nH_{2n}(OH)_2 + 2KC_2H_3O_2.$$

$$\underset{\substack{\text{a-Dibromethane.}\\\text{(Ethylenic bromide.)}}}{C_2H_4Br_2} + 2KC_2H_3O_2 = \underset{\text{Ethylenic acetate.}}{C_2H_4(C_2H_3O_2)_2} + 2KBr.$$

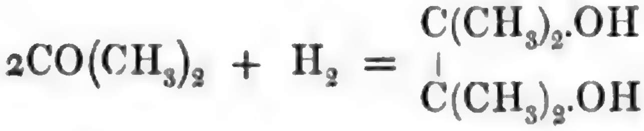
$$\underset{\text{Ethylenic acetate.}}{C_2H_4(C_2H_3O_2)_2} + 2KHO = \underset{\substack{\text{Glycol.}\\\text{(Ethylenic alcohol.)}}}{C_2H_4(OH)_2} + 2KC_2H_3O_2.$$

Usually the dibromoparaffins are employed, as they are far more readily acted upon, and also more readily prepared, than the dichloroparaffins; and, with one exception, all the alcohols obtained by this method have been prepared from the dibromoparaffins formed by combining the olefines with bromine. When argentic acetate is used to effect the conversion of the dihaloid paraffin into the diacetate, it is mixed with a small quantity of glacial acetic acid; the reaction usually takes place, if not at ordinary temperatures, on warming on the water bath. The saponification of the acetate is effected either by dry potassic hydrate, added in slight excess, or by a concentrated solution of baric hydrate.

A second general method of preparing glycols, which, however, gives rise only to glycols of a particular kind termed pinacones, consists in submitting the ketones of the $CO(C_nH_{2n+1})_2$ series to the action of nascent hydrogen:



$$2CO(C_nH_{2n+1})_2 + H_2 = \begin{array}{l} C(C_nH_{2n+1})_2.OH \\ | \\ C(C_nH_{2n+1})_2.OH \end{array}$$



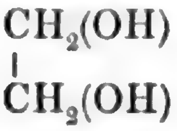
$$2CO(CH_3)_2 + H_2 = \begin{array}{l} C(CH_3)_2.OH \\ | \\ C(CH_3)_2.OH \end{array}$$

Acetone. Tetramethylglycol or pinacone.

(1493) *Classification of the Glycols.*—The glycols, like the binols, may be classified in several groups, according to their constitution. Glycols, such as the first term of the series, $(HO)H_2C.CH_2(OH)$, and propyleneglycol $(HO)H_2C.CH_2.CH_2(OH)$, in both of which the group $CH_2(OH)$, characteristic of the primary carbinols, is contained twice, are conveniently termed *primary glycols*; in a similar manner, those which contain the group $CH(OH)$ twice may be termed *secondary glycols*, and those in which no hydrogen atoms are associated with either of the carbon atoms to which the two OH groups are united may be designated *tertiary glycols*.

The following are examples of these three classes of glycols:

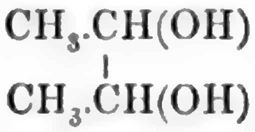
Primary glycol.



$$\begin{array}{l} CH_2(OH) \\ | \\ CH_2(OH) \end{array}$$

Glycol.

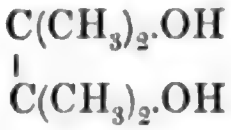
Secondary glycol.



$$\begin{array}{l} CH_3.CH(OH) \\ \quad\ \ | \\ CH_3.CH(OH) \end{array}$$

α-Dimethylglycol.

Tertiary glycol.

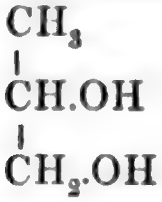


$$\begin{array}{l} C(CH_3)_2.OH \\ | \\ C(CH_3)_2.OH \end{array}$$

Tetramethylglycol.

But glycols which are in part primary, and in part secondary or tertiary, or in part secondary and in part tertiary, may also exist, such as, for example:

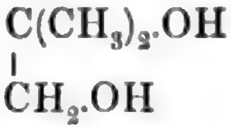
Primary-secondary.



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

Methylglycol.

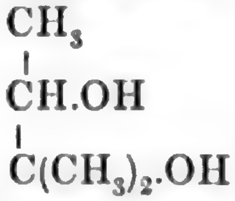
Primary-tertiary.



$$\begin{array}{l} C(CH_3)_2.OH \\ | \\ CH_2.OH \end{array}$$

β-Dimethylglycol.

Secondary-tertiary.



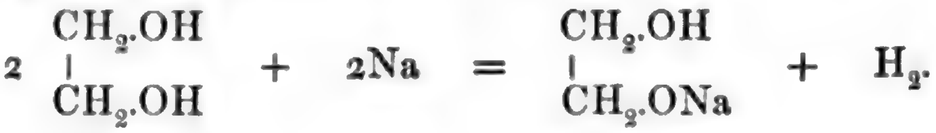
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ C(CH_3)_2.OH \end{array}$$

Trimethylglycol.

It is almost needless to state that each of these classes is divisible into sub-classes, according to the constitution of the radicles which are introduced in place of the hydrogen in glycol, &c.

(1494) *Properties of the Glycols.*—Although a considerable number of glycols have been prepared, our knowledge of most of them, and especially of their physical properties, and of their behaviour on oxidation, is extremely deficient. They are all colourless, odourless, more or less viscid fluids, soluble in water; the lower terms are sweet, but the higher terms are bitter, to the taste.

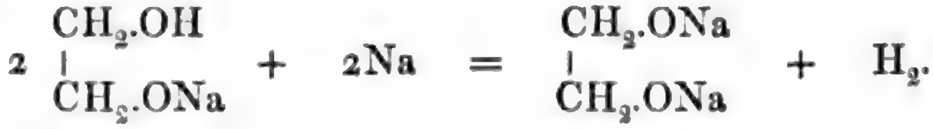
Sodium dissolves in the glycols with evolution of hydrogen, forming a mono-sodium derivative:



$$2\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array} + 2Na = \begin{array}{l}CH_2.OH\\ |\\ CH_2.ONa\end{array} + H_2.$$

Glycol. Sodium glycol.

By heating these compounds with sodium a second atom of hydrogen may be displaced; thus:



$$2\begin{array}{l}CH_2.OH\\ |\\ CH_2.ONa\end{array} + 2Na = \begin{array}{l}CH_2.ONa\\ |\\ CH_2.ONa\end{array} + H_2.$$

Sodium glycol. Disodium glycol.

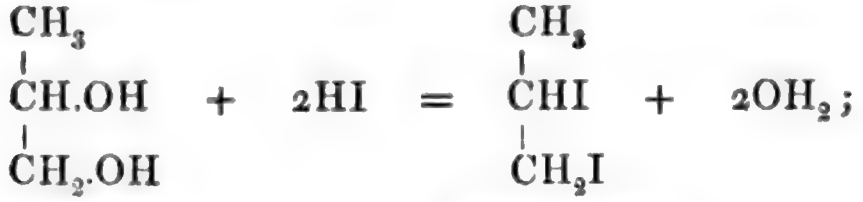
These sodium derivatives are decomposed by water, and the glycol re-formed.

By the action of gaseous hydrochloric or hydrobromic acid on the glycols, one of the OH groups is readily displaced by chlorine or bromine; monochlorinated and monobrominated derivatives of alcohols of the ethylic series, or glycolic chlor- and brom-hydrins are thus produced:

$$CH_3.CH(OH).CH_2(OH) + HCl = CH_3.CH(OH).CH_2Cl + OH_2.$$

Methylglycol. Chlorisopropylic alcohol.

These compounds are converted into dihaloid paraffin derivatives by the action of phosphorus pentachloride or pentabromide, and this change may also be partially effected by heating with a saturated solution of hydrochloric or hydrobromic acid. By the action of hydriodic acid, however, the glycols are readily converted into moniodo-paraffins, owing to the reduction by the hydriodic acid of the diiodoparaffins which are the immediate products of the action of hydriodic acid; thus:



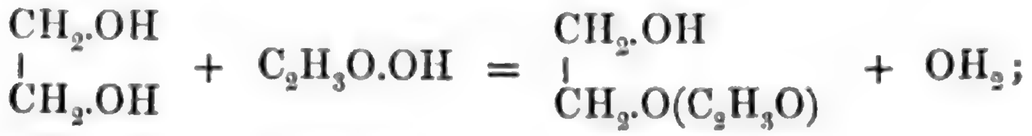
$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} + 2HI = \begin{array}{l}CH_3\\ |\\ CHI\\ |\\ CH_2I\end{array} + 2OH_2;$$

Methylglycol. β-Diiodopropane.

$$CH_3.CHI.CH_2I + HI = CH_3.CHI.CH_3 + I_2.$$

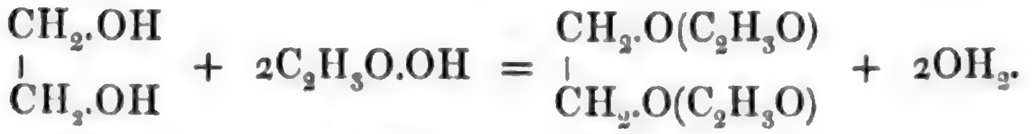
β-Diiodopropane. β-Iodopropane.

By heating the glycols with acids, such as acetic acid, ethereal salts are produced; the basic or the normal salt being formed according to the proportions employed:



$$\begin{array}{c} CH_2.OH \\ | \\ CH_2.OH \end{array} + C_2H_3O.OH = \begin{array}{l} CH_2.OH \\ | \\ CH_2.O(C_2H_3O) \end{array} + OH_2;$$

Glycol. Acetic acid. Basic ethylenic acetate. (Glycolic monacetin.)

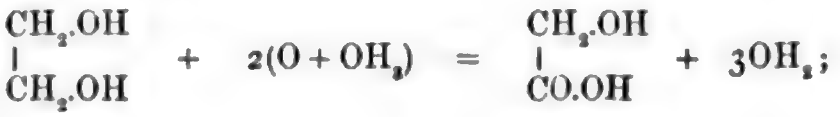


$$\begin{array}{c} CH_2.OH \\ | \\ CH_2.OH \end{array} + 2C_2H_3O.OH = \begin{array}{l} CH_2.O(C_2H_3O) \\ | \\ CH_2.O(C_2H_3O) \end{array} + 2OH_2.$$

Glycol. Acetic acid. Ethylenic acetate. (Glycolic diacetin.)

The oxidation of the glycols is usually effected with the aid of dilute nitric acid, but the isolation of the immediate products is extremely difficult on account of the readiness with which they undergo further oxidation.

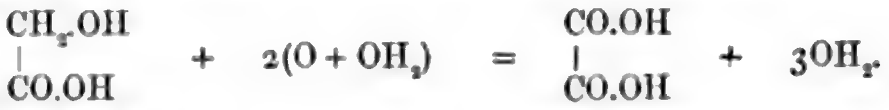
The primary glycols are apparently capable of furnishing two acids, each containing the same number of carbon atoms as the glycol oxidized—viz., in the first place, an acid of the glycolic series:



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array} + 2(O + OH_2) = \begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + 3OH_2;$$

Glycol. Glycolic acid.

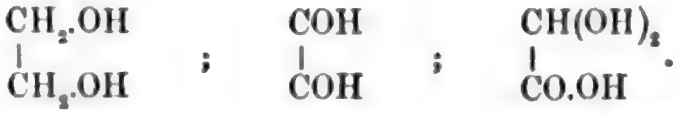
which on further oxidation is converted into the corresponding acid of the oxalic series:



$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + 2(O + OH_2) = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} + 3OH_2.$$

Glycolic acid. Oxalic acid.

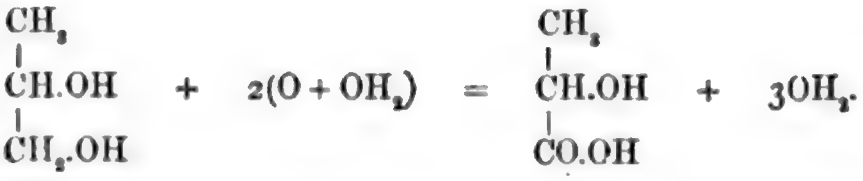
Intermediate products may also be formed, glycol, for example, yielding glyoxal and glyoxylic acid on oxidation, in addition to glycolic and oxalic acids; the relation of these bodies to glycol will be evident from the following formulæ:



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array} ; \begin{array}{l} COH \\ | \\ COH \end{array} ; \begin{array}{l} CH(OH)_2 \\ | \\ CO.OH \end{array} .$$

Glycol. Glyoxal. Glyoxylic acid.

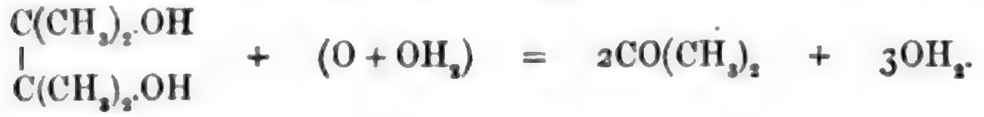
The primary-secondary glycols furnish acids of the glycolic series on oxidation, which, however, are not convertible into corresponding acids of the oxalic series; thus:



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 2(O + OH_2) = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + 3OH_2.$$

Methylglycol. Lactic acid.

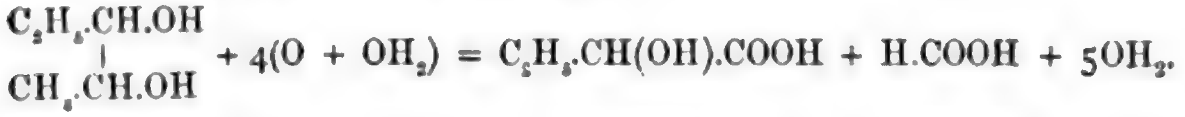
The tertiary glycols or pinacones are reconverted into ketones on oxidation:



$$\begin{array}{l} C(CH_3)_2.OH \\ | \\ C(CH_3)_2.OH \end{array} + (O + OH_2) = 2CO(CH_3)_2 + 3OH_2.$$

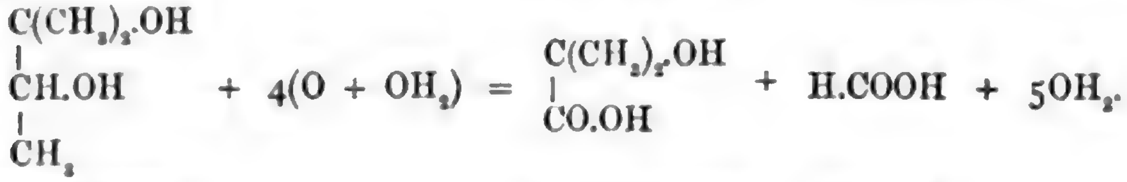
Tetramethylglycol. Acetone.

The probable behaviour of the secondary and secondary-tertiary glycols is illustrated by the following equations:



$$\begin{array}{l} C_2H_5.CH.OH \\ \quad | \\ CH_3.CH.OH \end{array} + 4(O + OH_2) = C_2H_5.CH(OH).COOH + H.COOH + 5OH_2.$$

Ethylmethylglycol. a-Oxybutyric acid. Formic acid.



$$\begin{array}{l} C(CH_3)_2.OH \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + 4(O + OH_2) = \begin{array}{l} C(CH_3)_2.OH \\ | \\ CO.OH \end{array} + H.COOH + 5OH_2.$$

Trimethylglycol. Oxyisobutyric acid. Formic acid.

(1495) METHALDEHYDROL: $CH_2(OH)_2$.—When diiodomethane or methylenic iodide is heated with argentic acetate and a small quantity of glacial acetic acid, it is converted into the diacetate $CH_2(C_2H_3O_2)_2$; on heating this substance with water in closed tubes at 100° (212° F.) it is dissolved and decomposed, and a solution is obtained which it can scarcely be doubted contains the compound $CH_2(OH)_2$ together with acetic acid:

$$CH_2(C_2H_3O_2)_2 + 2OH_2 = CH_2(OH)_2 + 2HC_2H_3O_2.$$

On evaporating the solution in vacuo, however, a white solid substance remains which is a polymeride of methylic or formic aldehyde, probably of the composition $C_3H_6O_3$ (see Formic Aldehyde); this substance is insoluble in water, but when it is heated with water at 130°—150° (266°—302° F.) in closed vessels it dissolves, probably being converted into methaldehydrol (Butlerow, *Ann. Chem. Pharm.*, cvii. 110; cxi. 242; cxv. 326):

$$C_3H_6O_3 + 3OH_2 = 3CH_2(OH)_2.$$

The solution of methaldehydrol is readily oxidized, formic acid being produced on adding to it freshly precipitated argentic oxide (argentic hydrate):

$$CH_2(OH)_2 + 2AgOH = H.COOH + 2Ag + 2OH_2.$$

(1496) GLYCOL OR ETHYLENIC ALCOHOL: $C_2H_4(OH)_2 = 62$.—This compound was discovered in 1856 by Wurtz, who prepared it from ethylenic iodide; it may be obtained from the corresponding dichlor- or dibromethane in the manner already described, and it is also formed on heating dibromomethane, CH_2Br_2, with water and plumbic oxide to 140°—150° (284°—302° F.) (Jeltekow, *Deut. chem. Ges. Ber.*, vi. 558), but according to Demole (*Ann. Chem. Pharm.*, clxxiii. 117; clxxvii. 45; *Deut. chem. Ges. Ber.*, ix. 480, 636, 917), it is most readily prepared by heating a mixture of α-dibromethane or ethylenic bromide with potassic acetate and aqueous alcohol.

The proportions employed, the strength of the alcohol, and the length of time during which the mixture is heated are all of consequence: the most favourable result being obtained when a mixture of ethylenic bromide and carefully *dried* potassic acetate in the proportions $C_2H_4Br_2 : KC_2H_3O_2 = 188 : 98$ with an amount of alcohol of 91 per cent. (sp. gr. ·82), about equal in weight to the ethylenic bromide employed, is heated to boiling for about twenty hours in a flask attached to a reversed condenser; after filtering off the potassic bromide, the glycol is isolated from the liquid by fractional distillation.

Nearly one-half the ethylenic bromide is recovered, but it is not therefore to be supposed that one-half the amount will suffice; on the contrary, when a mixture of the bromide and acetate in the proportions $C_2H_4Br_2 : 2KC_2H_3O_2 = 188 : 196$, with alcohol of 91 per cent. is similarly treated, only glycol monacetin, $C_2H_4(OH).C_2H_3O_2$, is obtained.

The formation of glycol from ethylenic bromide, potassic acetate, and aqueous alcohol is undoubtedly the end result of a series of changes, and it is difficult to pronounce with certainty upon their nature and the precise order in which they occur. It may be supposed that when the bromide and acetate are heated together in the proportion of one molecule of the former to two of the latter a certain amount of the bromide is converted into the diacetin, which is then decomposed by the alcohol and converted into the monacetin, this reaction being perhaps in part effected by the alcohol itself and in part by the water which it contains; thus:

$$C_2H_4Br_2 + 2KC_2H_3O_2 = C_2H_4(C_2H_3O_2)_2 + 2KBr;$$
$$C_2H_4(C_2H_3O_2)_2 + C_2H_5.OH = C_2H_4(OH).C_2H_3O_2 + C_2H_5.C_2H_3O_2;$$
$$C_2H_4(C_2H_3O_2)_2 + OH_2 = C_2H_4(OH).C_2H_3O_2 + HC_2H_3O_2.$$

In this manner, if the heating be continued sufficiently long, the whole of the ethylenic bromide ultimately becomes converted into glycolic monacetin.

When the larger proportion of ethylenic bromide is employed, it is probable that, until the whole of the potassic acetate is acted upon, only monacetin is produced, but that then the following reactions occur in succession:

$$\alpha \quad C_2H_4Br_2 + C_2H_4(OH).C_2H_3O_2 = C_2H_4Br(OH) + C_2H_4Br(C_2H_3O_2);$$
$$\beta \quad C_2H_4Br(C_2H_3O_2) + C_2H_5.OH = C_2H_4Br(OH) + C_2H_5.C_2H_3O;$$
$$\gamma \quad C_2H_4Br(OH) + OH_2 = C_2H_4(OH)_2 + HBr.$$

A certain amount of hydrobromic acid is thus produced, which probably at once enters into reaction with the monacetin present to form bromacetin and water:

$$C_2H_4(OH).C_2H_3O_2 + HBr = C_2H_4Br(C_2H_3O_2) + OH_2;$$

and from the bromacetin thus formed, the bromhydrin $C_2H_4Br(OH)$ and glycol are then produced in succession by the reactions indicated by equations β and γ. hydrobromic acid being again liberated. In this manner, the conversion of a large amount of glycolic monacetin into glycol may be gradually effected by the aid of a very small amount of hydrobromic acid. According to Demole, 25 grams of glycolic monacetin are almost completely converted into glycol by boiling with 80 per cent. alcohol and 2 *or* 3 *drops* of the bromhydrin $C_2H_4Br(OH)$ for twenty hours.

Glycol may also be prepared by boiling glycolic monacetin with ethylenic bromide and alcohol of 91 per cent.; the rapidity with which the change is effected depends, however, upon the amount of bromide employed. Thus the conversion of 200—225 grams of the monacetin is completed in twenty-four hours if it be mixed with 100 grams of ethylenic bromide, but if 50 grams of the bromide are taken the boiling must be continued for thirty-six hours, and if only 25 grams of the bromide are added it requires at least forty-five hours' boiling to effect the conversion (Demole).

According to Zeller and Huefner (*Journ. pr. Chem.* [2], x. 270), ethylenic bromide is readily converted into glycol by boiling with an aqueous solution of potassic carbonate.

Glycol is a colourless, almost odourless liquid, of the consistence of a thin syrup; it has a sweet alcoholic taste. It boils at 197° (386°·6 F.), and at 0° (32° F.) has the sp. gr. 1·125; it is miscible with water and alcohol in all proportions. When a solution of glycol is exposed to air or oxygen in contact with platinum black, *glycolic acid*, $CH_2(OH).COOH$, is produced; on oxidation with nitric acid, glycol furnishes glycolic, glyoxylic, and oxalic acids, and glyoxal (p. 508). By heating to 250° (482° F.) with potassic hydrate, it is converted into potassic oxalate:

$$CH_2(OH).CH_2(OH) + 2KOH = CO(OK).CO(OK) + 4H_2.$$

When it is gently heated with zincic chloride, it furnishes ethylic or acetic aldehyde (Wurtz), and according to Nevolé (*Compt. Rend.*, lxxxiii. 228), a small amount of aldehyde is also produced when glycol is heated with water to 220°—230° (428—446° F.)*:

$$\underset{\text{Glycol.}}{CH_2(OH).CH_2(OH)} - OH_2 = \underset{\text{Ethylic aldehyde.}}{CH_3.COH.}$$

By the action of hydrochloric acid on glycol, monochlorethylic alcohol or glycolic chlorhydrin, $C_2H_4Cl(OH)$, is produced: this compound may also be prepared by the action of an excess of sulphur chloride, S_2Cl_2, on glycol (Carius, *Ann. Chem. Pharm.*, cxxiv. 257). It is a colourless liquid soluble in water, which boils at about 130° (266° F.). The corresponding bromo-derivative, $C_2H_4Br(OH)$, boils at 147° (296°·6 F.); it may be obtained by the action of hydrobromic acid on glycol, by combining ethylenic oxide, C_2H_4O, with hydrobromic acid, or by heating a mixture of ethylenic bromide and glycol to 120° (248° F.). When hydriodic acid gas is passed into glycol, it is rapidly absorbed and much heat is developed, ethylenic iodide, $C_2H_4I_2$, being produced; but when the temperature is prevented from rising by cooling the vessel which contains the glycol, the intermediate compound, $C_2H_4I(OH)$, is formed, which may also be obtained by heating the corresponding chlorinated compound with potassic iodide. It is a colourless liquid which decomposes on distillation, yielding ethylenic iodide and, probably, glycol. Glycol is readily acted upon by acetic chloride and converted into chlorethylic acetate or glycolic chloracetin:

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* According to Carius (*Ann. Chem. Pharm.*, cxxxi. 173), aldehyde is obtained on heating ethylenic bromide with water to 150°—160° (302°—320° F.). When ethylenic chloride is heated with water and plumbic oxide to 170° (338° F.) glycol is formed, and it is therefore probable that the formation of aldehyde from ethylenic bromide is dependent upon the presence of hydrobromic acid (Jeltekow, *Deut. chem. Ges. Ber.*, vi. 558). When β-dibromopropane or propylenic bromide is heated with water and plumbic oxide to 170° (338° F.), acetone is produced, but β-dichloropropane on similar treatment furnishes both propylenic glycol and acetone (Jeltekow, comp. p. 437).

$$C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + 2C_2H_3OCl = C_2H_4\left\{\begin{matrix}Cl\\C_2H_3O_2\end{matrix}\right. + C_2H_4O_2 + HCl.$$

In a similar manner, many of the secondary and the tertiary carbinols are converted into chloroparaffins by the action of acetic chloride (Flavitzsky, *Ann. Chem. Pharm.*, clxxix. 364).

(1497) *Polyethlyenic Glycols.*—By heating glycol with ethylenic oxide, or with ethylenic bromide, a series of compounds which may be termed polyethylenic glycols have been obtained by Wurtz and Lourenco, which are formed by the condensation of *n* molecules of glycol with elimination of $n - 1$ molecules of water. The following have been isolated:

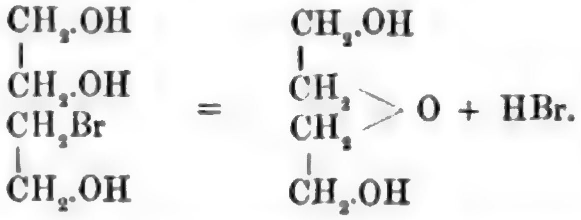
Diethylenic glycol . . $C\,H_{10}O_3 = 2C_2H_4(OH)_2 - OH_2$
Triethylenic „ . . $C_6H_{14}O = 3C_2H_4(OH)_2 - 2OH_2$
Tetrethylenic „ . . $C_8H_{18}O_5 = 4C_2H_4(OH) - 3OH_2$
Pentethylenic „ . . $C_{10}H_{22}O_6 = 5C_2H_4(OH)_2 - 4OH_2$
Hexethylenic „ . . $C_{12}H_{26}O_7 = 6C_2H_4(OH)_2 - 5OH_2$.

In preparing these bodies from glycol and ethylenic bromide, the mixture of the two substances is heated to 110°—120° (230°—248° F.) in sealed tubes: as to which compounds are produced depends both upon the proportions taken, and the length of time during which the heating is continued, but if a sufficient excess of glycol is employed still higher members of the series than those above mentioned may be obtained. The products are separated by fractional distillation, the distillation of the higher terms being effected under reduced pressure.

The first reaction which occurs undoubtedly consists in the formation of glycolic bromhydrin; thus:

$$C_2H_4(OH)_2 + C_2H_4Br_2 = 2C_2H_4Br(OH).$$

From this compound and glycol, diethylenic glycol is then produced in the manner represented by the following equation:



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\\ CH_2Br\\ |\\ CH_2.OH\end{array} = \begin{array}{l}CH_2.OH\\ |\\ CH_2\\ CH_2\\ |\\ CH_2.OH\end{array}\!\!>O + HBr.$$

The hydrobromic acid thus liberated serves to convert a further quantity of glycol into the bromhydrin, which then enters into reaction with the diethylenic glycol, and in a similar manner converts it into triethylenic glycol, hydrobromic acid being again liberated; by a similar cycle of reactions tetrethylenic glycol is formed from triethylenic glycol, pentethylenic glycol from tetrethylenic glycol, and hexethylenic glycol from pentethylenic glycol. If the temperature is allowed to rise above 130° (266° F.) the hydrobromic acid produced not only acts on the glycol, but also on the polyethylenic glycols, and bromhydrins of the latter are formed.

Diethylenic Glycol: $C_4H_8O(OH)_2$, is a sweet syrupy liquid, soluble in water, alcohol, and ether; it boils at about 245° (473° F.). On oxidation with nitric acid, it furnishes *diglycolic acid:*

$$\underset{\text{Diethylenic glycol.}}{CH_2(OH).CH_2.O.CH_2.CH_2(OH)} \quad ; \quad \underset{\text{Diglycolic acid.}}{COOH.CH_2.O.CH_2.COOH.}$$

Triethylenic Glycol: $C_6H_{12}O_2(OH)_2$, is a very thick liquid, which boils at about 290° (654° F.). Nitric acid converts it into *diglycolethylenic acid:*

$$\underset{\text{Triethylenic glycol.}}{CH_2(OH).CH_2.O.CH_2.CH_2.O.CH_2.CH_2(OH).}$$

$$\underset{\text{Diglycolethylenic acid.}}{COOH.CH_2.O.CH_2.CH_2.O.CH_2.COOH.}$$

The higher polyethylenic glycols are still more viscid substances; the three remaining terms which have been isolated boil respectively at about 230° (446° F.), 280° (536° F.), and 325° (617° F.) under a pressure of 25 mm. of mercury.

(1498) TRICHLORETHALDEHYDROL or *Chloral-hydrate:* $CCl_3.CH(OH)_2$.—This compound is formed by the combination of trichloraldehyde or chloral with water: $CCl_3.COH + OH_2 = CCl_3.CH(OH)_2$, which is attended with the development of a considerable amount of heat. It may also be produced by the action of chlorine on a well cooled aqueous solution of aldehyde (Wurtz and Vogt, *Compt. Rend.*, lxxiv. 777; Pinner, *Ann. Chem. Pharm.*, clxxix. 24); its formation in this manner may be regarded as evidence of the presence of the compound $CH_3.CH(OH)_2$ in such a solution, and is not to be accounted for by the assumption that the aldehyde, $CH_3.COH$, is converted into chloral, which then combines with the water, as chloral is never obtained when aldehyde alone is submitted to the action of chlorine (see Aldehyde):

$$\underset{\text{Ethaldehydrol.}}{CH_3.CH(OH)_2} + 3Cl_2 = \underset{\text{Trichlorethaldehydrol.}}{CCl_3.CH(OH)_2} + 3HCl.$$

It crystallizes in large monoclinic prisms, soluble in water; it melts at 46° (114°·8 F.), and boils at about 96° (204°·8 F.): but its vapour consists of a mixture of chloral and water.

On mixing chloral with glacial acetic acid, heat is developed, and when the liquid is allowed to evaporate over sulphuric acid, crystals are obtained which sometimes consist of ordinary chloral-hydrate, but sometimes of a substance of the same composition, melting at 80° (176° F.); the relation of this substance to ordinary chloral-hydrate has not yet been ascertained (Meyer and Dulk, *Ann. Chem. Pharm.*, clxxi. 74).

Chloral-hydrate is converted by oxidation with concentrated nitric acid into trichloracetic acid:

$$CCl_3.CH(OH)_2 + (O + OH_2) = CCl_3.COOH + 2OH_2.$$

On treatment with aqueous alkalies, it furnishes trichloromethane or chloroform and a formate:

$$2CCl_3.CH(OH)_2 + KHO = CHCl_3 + H.COOK + OH_2.$$

It readily parts with the elements of a molecule of water when agitated with concentrated sulphuric acid, and is converted into chloral. On passing sulphuretted hydrogen gas into a concentrated aqueous solution of chloral-hydrate the following reaction occurs:

$$2CCl_3.CH(OH)_2 + SH_2 = [CCl_3.CH.OH]_2S + 2OH_2.$$

The compound $[CCl_3.CH.OH]_2S$ is a white crystalline solid, insoluble in water, which gradually decomposes it, but soluble in alcohol, benzene, &c.; it melts at 128° (262°·4 F.), and is converted by acetic chloride into the compound $[CCl_3.CH.C_2H_3O_2]_2S$, which melts at 78° (172°·4 F.) (Paterno, Wyss, *Journ. Chem. Soc.*, xxvii. 459).

By the action of acetic chloride on chloral-hydrate the chloracetin $CCl_3.CHCl(C_2H_3O_2)$ is produced; the formation of this body may be supposed to take place in the same manner as that of the compound $CH_2Cl.CH_2(C_2H_3O_2)$ from glycol (p. 512), but it appears more probable that the first action of the chloride consists in the production of chloral, which then unites with a molecule of acetic chloride; thus:

$$\underset{\text{Chloral-hydrate.}}{CCl_3.CH(OH)_2} + \underset{\text{Acetic chloride.}}{C_2H_3OCl} = \underset{\text{Chloral.}}{CCl_3.COH} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + HCl.$$

$$CCl_3.COH + C_2H_3OCl = CCl_3.CHCl(C_2H_3O_2).$$

It has been shown that the reaction represented by the second of these equations readily takes place (Meyer and Dulk, *Ann. Chem. Pharm.*, clxxi. 67).

Chloral-hydrate is chiefly remarkable on account of its physiological action, producing deep sleep when administered by the mouth, or when directly introduced into the circulation by subcutaneous injection. The hypnotic action which it exercises has been attributed to its conversion into chloroform within the system, the latter being regarded as the really active substance, but there appears to be much reason to doubt this explanation (comp. Tomaszcwicz, *Journ. Chem. Soc.*, xxvii. 824; Mering and Musculus, *Deut. chem. Ges. Ber.*, viii. 662). Chloral-hydrate is decomposed in presence of potassic hydrate by potassic permanganate, carbonic oxide gas being evolved, and potassic chloride, formate, and carbonate produced: the reaction occurs even with very dilute solutions, and if borax be substituted for potassic hydrate. This circumstance has led Tauret to suggest that chloral-hydrate undergoes a similar decomposition in the circulation, and that its action as an hypnotic is due to the carbonic oxide produced (*Compt. Rend.*, lxxix. 662). A crystalline monobasic acid of the composition $C_7H_{12}Cl_2O_6$, called *urochloralic acid*, has been isolated from the urine of persons who were taking four to five grams of chloral-hydrate per diem; it exerts a lævorotatory action on polarized light, and reduces an alkaline cupric solution (Mering and Musculus, *loc. cit.*).

Dichloraldehyde and dibrom- and tribromaldehyde combine with water forming compounds which both in composition and properties exhibit the closest analogy to trichlorethaldehydrol. *Dichlorethaldehydrol*, $CHCl_2.CH(OH)_2$, is also one of the products of the action of chlorine on an aqueous solution of aldehyde; it crystallizes in laminæ. *Dibromethaldehydrol*, $CHBr_2.CH(OH)_2$, crystallizes in fine needles; *tribromethaldehydrol*, $CBr_3.CH(OH)_2$, forms broad rhombic plates which melt at 53° (127°·4 F.) (Pinner, *Ann. Chem. Pharm.*, clxxix. 67).

(1499) ALCOHOLS OF THE COMPOSITION $C_3H_6(OH)_2 = 76$.—*Primary* or *α-Propylenic glycol:* $CH_2(OH).CH_2.CH_2(OH)$, prepared from α-dibromopropane (1189), boils at 216°—217° (420°·8—422°·6 F.). If it is saturated with hydrochloric acid gas, and the mixture is heated to 100° (212° F.) for 5—6 hours, a mixture of α-dichloropropane and *α-chloropropylic alcohol*, $CH_2Cl.CH_2.CH_2(OH)$, is produced. The latter is an oily liquid, soluble in water, of the specific gravity 1·132 at 17° (62°·6 F.), and boils at 160° (320° F.) (Reboul, *Compt. Rend.*, lxxviii. 1773; lxxix. 169).

β-Propylenic glycol or *Methylglycol:* $CH_3.CH(OH).CH_2(OH)$, prepared from β-dibromopropane or propylenic bromide, $CH_3.CHBr.CH_2Br$, is a colourless oily liquid, of sweet taste; it boils at 188° (370°·4 F.), and at 0° (32° F.) has the specific gravity 1·051. It is miscible in all proportions with water and alcohol. When a solution of methylglycol is exposed to the air in contact with spongy platinum, lactic acid is produced (Wurtz):

$$CH_3.CH(OH).CH_2(OH) + 2(O + OH_2) = CH_3.CH(OH).COOH + 3OH_2;$$

but even very dilute nitric acid oxidizes it to glycolic acid:

$$CH_2(OH).CH(OH).CH_3 + 5(O + OH_2) = CH_2(OH).COOH + CO_2 + 7OH_2.$$

When oxidized by a solution of potassic permanganate, however, it furnishes acetic acid:

$$CH_3.CH(OH).CH_2(OH) + 4(O + OH_2) = CH_3.COOH + CO_2 + 6OH_2,$$

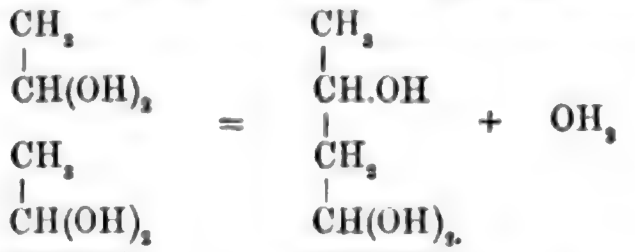
and by heating it with potassic hydrate to 250° (482° F.), chiefly potassic oxalate is produced.

On distilling it with zincic chloride, propylic aldehyde, $CH_3.CH_2.COH$, is obtained.

By the action of hydrochloric acid gas, methylglycol is converted into a chloropropylic alcohol boiling at 127° (260°·6 F.), of the specific gravity 1·1302 at 0° (32° F.) (Oser, *Ann. Chem. Pharm. Supp.*, i. 253). According to Markownikoff (*ibid.*, cliii. 251), a body having the same properties is obtained by combining propylene with hypochlorous acid, and it has already been pointed out (p. 462) that there is reason to suppose that the compound so produced has the constitution represented by the formula $CH_3.CHCl.CH_2(OH)$. It is remarkable, however, that the isomeric compound, (?) $CH_3.CH(OH).CH_2Cl$, obtained by Oppenheim (p. 204), is stated to boil at the same temperature. By combining propylenic oxide with hydrobromic and hydriodic acid, Markownikoff obtained corresponding bromo- and iodopropylic alcohols; the former boils at 145°—148° (293°—298°·4 F.), and the latter at 105° (221° F.) under a pressure of 60 mm. By the action of hydriodic acid, methylglycol is converted into β-iodopropane or isopropylic iodide (Wurtz).

(1500) ALCOHOLS OF THE COMPOSITION $C_4H_8(OH)_2 = 90$.—Three of the six possible isomeric butylenic glycols have been obtained, but very imperfectly studied.

Methyl-α-propylenic glycol: $CH_3.CH(OH).CH_2.CH_2(OH)$, is produced, although in very small quantity and together with ethylic alcohol, on treating an acidulated aqueous solution of ethylic aldehyde with sodium amalgam, hydrochloric acid being added from time to time so as always to maintain the liquid slightly acid (Kekulé, *Deut. chem. Ges. Ber.*, v. 56); it is more readily obtained by treating a solution of aldol or oxybutyric aldehyde in a similar manner (Wurtz, *Compt. Rend.*, lxxvi. 1165). Its formation from aldehyde, or rather from aldehydrol, which first undergoes condensation and is converted into aldol-hydrate or oxybutaldehydrol, may be represented by the following equations:



$$\begin{array}{c} CH_3 \\ | \\ CH(OH)_2 \\ \\ CH_3 \\ | \\ CH(OH)_2 \end{array} = \begin{array}{c} CH_3 \\ | \\ CH.OH \\ | \\ CH_2 \\ | \\ CH(OH)_2. \end{array} + OH_2$$

Aldehydrol. Aldol-hydrate.

$$CH_3.CH(OH)CH_2.CH(OH)_2 + H_2 = CH_3.CH(OH).CH_2.CH_2(OH) + OH_2.$$

It is a syrupy liquid, of sweet but slightly pungent taste, and boils at about 204° (399°·2 F.). On oxidation with nitric acid, it furnishes acetic and oxalic acids, and much acetic acid is also produced when a solution of chromic acid is employed; in both cases appreciable quantities of ethylic aldehyde and of crotonic aldehyde, $CH_3.CH=CH.COH$, are formed.

Ethylglycol: $C_2H_5.CH(OH).CH_2(OH)$, prepared from the dibromotetrane obtained by combining normal butylene with bromine, is a syrupy liquid of sweet but somewhat pungent taste; it boils at about 192° (377°·6 F.), and at 0° (32° F.) has the specific gravity 1·0189. On oxidation with nitric acid, it appears to furnish only glycolic acid and glyoxylic acid, $CH(OH)_2.COOH$ (Grabowsky and Saytzeff, *Ann. Chem. Pharm*, clxxix. 332).

Dimethylglycol: $(CH_3)_2C(OH).CH_2(OH)$, is formed by boiling the isomeric dibromotetrane produced from isobutylene or β-dimethylethylene, $CH_2=C(CH_3)_2$, and bromine, with an aqueous solution of potassic carbonate. It boils at about 177° (350°·6 F.), and at 0° (32° F.) has the specific gravity 1·0129. When it is oxidized by a solution of potassic permanganate, acetic acid is formed, but its behaviour with nitric and chromic acids is peculiar, a liquid body being produced which approximately has the composition represented by the formula $C_6H_{12}O_2$ (Nevolé, *Compt. Rend.*, lxxxiii. 65; 146).

Trichlorobutaldehydrol: $C_3H_4Cl_3.CH(OH)_2$.—This compound is formed by the combination of the trichlorobutylic aldehyde produced by the action of chlorine on aldehyde (see Ethylic aldehyde) with water. In all respects it exhibits the closest resemblance to chloral-hydrate, crystallizing from water in thin, glistening, white plates, which melt at 78° (172°·4 F.). On oxidation with nitric acid, it yields trichlorobutyric acid, $C_4H_5Cl_3O_2$; and on treatment with alkalies, it is apparently decomposed in the following manner:

$$C_3H_4Cl_3.CH(OH)_2 \ + \ KHO \ = \ C_3H_5Cl_3 \ + \ H.COOK \ + \ OH_2,$$

but the trichloropropane thus formed is further acted upon by the alkali and converted into a dichloropropylene, $C_3H_4Cl_2$ (Krämer and Pinner, *Ann. Chem. Pharm.*, clviii. 45; Pinner, *ibid.*, clxxix. 26, 38).

(1501) ALCOHOLS OF THE COMPOSITION $C_5H_{10}(OH)_2 = 104$.—Only three of the many possible isomeric amylenic glycols have been obtained.

Isopropylglycol: $C_3H_7{}^{\beta}.CH(OH).CH_2(OH)$, prepared from the dibromopentane formed by combining the amylene from the iodide of isoprimary fermentation amylic alcohol with bromine, is a thick liquid, pungent and bitter to the taste, soluble in water in all proportions; it boils at 206° (402°·8 F.), and at 0° (32° F.) has the specific gravity ·9987. On oxidation with nitric acid, it appears to furnish *oxyvalerianic* acid, $C_3H_7{}^{\beta}.CH(OH).COOH$ (Flavitzsky, *ibid.*, clxxix. 351).

Ethylmethylglycol: $C_2H_5.CH(OH).C(CH_3)H.OH$, is furnished by the dibromopentane formed from the amylene from the iodide of diethylcarbinol. It closely resembles the preceding glycol, but boils at about 188° (370°·4 F.), and at 0° (32° F.) has the specific gravity ·9945. On oxidation with nitric acid, it appears to furnish a small quantity of α-oxybutyric acid, $CH_3.CH_2.CH(OH).COOH$, together with formic, acetic, and glycolic acids (Wagner and Saytzeff, *ibid.*, clxxix. 307).

Trimethylglycol: $(CH_3)_2C(OH).CH(CH_3)(OH)$, prepared from the bromide of ordinary amylene or trimethylethylene, is a syrupy liquid of bitter taste; it boils at 177° (350°·6 F.), and at 0° (32° F.) has the specific gravity ·987 (Wurtz). On oxidation with nitric acid, it furnishes oxyisobutyric acid, $(CH_3)_2C(OH).COOH$ (Wurtz, *ibid.*, cvii. 197; Markownikoff, *ibid.*, cliii. 228).

The behaviour on oxidation of the two glycols from the amylenes prepared from fermentation amylic alcohol is of importance, as it establishes the constitution of the olefines from which they are produced. Thus, the simplest and most probable formula which can be attributed to the amylene from the iodide of isoprimary amylic alcohol (p. 194) is that which represents it as isopropylethylene: $C_3H_7^{\beta}.HC{=}CH_2$, and this formula is confirmed by the production of an acid of the composition $C_3H_7^{\beta}.CH(OH).COOH$ on oxidation of the glycol prepared from the amylene in question. On the other hand, the formula $C(CH_3)_2{=}CH.CH_3$ for the amylene produced from the fermentation alcohol by the action of zincic chloride is not only that which best accords with its general behaviour, and which enables us to explain its formation (p. 451), but it is the only one which enables us to account for the formation of oxyisobutyric acid, $(CH_3)_2C(OH).COOH$, by the oxidation of the glycol derived from it.

(1502) ALCOHOLS OF THE COMPOSITION $C_6H_{12}(OH)_2 = 118$.—*Dimethyl-a-butylenic glycol:* $CH_3.CH(OH).CH_2.CH_2.CH(OH).CH_3$, prepared from the diiodhexane produced by combining the hydrocarbon diallyl (1255) with hydriodic acid, is a syrupy liquid, soluble in water; it boils at 212°—215° (413°·6—419° F.), and at 0° (32° F.) has the specific gravity ·9638. By heating with a concentrated solution of hydrochloric acid to 100° (212° F.), it is converted into dichlorhexane, $C_6H_{12}Cl_2$, and a solution of hydriodic acid acts upon it in a similar manner at ordinary temperatures (Wurtz, *ibid.*, cxxxi. 344).

Propylmethylglycol: $C_3H_7^{\alpha}.CH(OH).CH(OH).CH_3$.—The glycol prepared from the bromide of the hexylene from mannite (pp. 195, 399) probably has this constitution. It is a colourless syrup, miscible with water in all proportions; it boils at about 207° (404°·6 F.), and at 0° (32° F.) has the specific gravity ·9669. It is not converted into the corresponding dichloroparaffin by the action of hydrochloric acid at 100° (212° F.), but furnishes a product boiling between 100° and 250° (212° and 482° F.); hydriodic acid converts it into normal secondary hexylic iodide (Wurtz, *ibid.*, cxxxiii. 217).

Tetramethylglycol or *pinacone:* $(CH_3)_2C(OH).C(CH_3)_2.OH$, is produced, together with isopropylic alcohol, by the action of nascent hydrogen on dimethylketone or acetone, $CH_3.CO.CH_3$. It crystallizes from water in large plates of the composition $C_6H_{12}(OH)_2 + 6OH_2$, which melt at 42° (107°·6 F.). The anhydrous glycol, which may be obtained by distilling this substance, is also crystalline; it melts at 38° (100°·4 F.), and boils at about 172° (341°·6 F.). On oxidation with chromic acid, pinacone is reconverted into acetone; its conversion into pinacolin by the action of concentrated sulphuric acid has already been noticed (p. 453).

(1503) HIGHER HOMOLOGUES OF GLYCOL.—An *octylenic glycol*, probably of the composition $C_5H_{11}^{\alpha}.CH(OH).CH(OH).CH_3$, has been prepared from the dibromoctane from octylene (1235); it is an oily liquid, insoluble in water, of the specific gravity ·932 at 0° (32° F.), and boils at 235°—240° (455°—464° F.) (Clermont, *ibid.*, *Supp.*, iii. 254; clvi. 118).

The remaining terms of the series are all tertiary glycols. A crystalline *dipropyldimethylglycol* is obtained by the action of nascent hydrogen on methylpropylketone; it boils at 225°—230° (437°—446° F.) (Grimm, *ibid.*, clvii. 257). The isomeric *dimethyldiisopropylglycol* is apparently a liquid (Münch, *ibid.*, clxxx. 340).

A crystalline *dimethyldibutylglycol* is formed on submitting pinacolin or methyl tertiary-butylketone to the action of nascent hydrogen; it melts at 69° (156°·2 F.) (Friedel and Silva, *Compt. Rend.*, lxxvi. 226).

Lastly, dipropylketone is converted by nascent hydrogen into a *tetrapropylglycol* which melts at 68° (154°·4 F.); it is reconverted into the ketone by oxidation (Kurtz, *Ann. Chem. Pharm.*, clxi. 215). The isomeric *tetraisopropylglycol* is liquid (Münch).

$CH_2.OH$ | $CH_2.OH$ B.P. 197°						
$CH_2.OH$ | CH_2 | $CH_2.OH$ B.P. 216°—217°	CH_3 | $CH.OH$ | $CH_2.OH$ B.P. 188°					
$CH(CH_3).OH$ | CH_2 | $CH_2.OH$ B.P. 204°	C_2H_5 | $CH.OH$ | $CH_2.OH$ B.P. 192°		$C(CH_3)_2.OH$ | $CH_2.OH$ B.P. 177°			
	$C_3H_7^{\beta}$ | $CH.OH$ | $CH_2.OH$ B.P. 206°	$CH(C_2H_5).OH$ | $CH(CH_3).OH$ B.P. 188°	$C(CH_3)_2.OH$ | $CH(CH_3).OH$ B.P. 177°			
	$CH(CH_3).OH$ | CH_2 | CH_2 | $CH(CH_3).OH$ B.P. 212°—215°	$CH(C_3H_7)^{\alpha}.OH$ | $CH(CH_3).OH$ B.P. 207°		$C(CH_3)_2.OH$ | $C(CH_3)_2.OH$ B.P. 172°. M.P. 46°		
		$CH(C_5H_{11})^{\alpha}.OH$ | $CH(CH_3).OH$ B.P. 235°—240°				
				$C(CH_3)(C_3H_7)^{\alpha}.OH$ | $C(CH_3)(C_3H_7)^{\alpha}.OH$ B.P. 225°—230°	$C(CH_3)(C_3H_7)^{\beta}.OH$ | $C(CH_3)(C_3H_7)^{\beta}.OH$ B.P. ?	
						$C(CH_3)(C_4H_9)^{\delta}.OH$ | $C(CH_3)(C_4H_9)^{\delta}.OH$ M. P. 69
				$C(C_3H_7)_2^{\alpha}.OH$ | $C(C_3H_7)_2^{\alpha}.OH$ M.P. 68°	$C(C_3H_7)_2^{\beta}.OH$ | $C(C_3H_7)_2^{\beta}.OH$ B.P. ?	

(1504) On comparing together, with the aid of the table on the previous page, the glycols which are strictly homologous, it will be evident that no relation is at present discernible between their boiling points, with the exception that the difference between the only two primary glycols in the table is the same as obtains in the case of the normal primary alcohols of the ethylic series; but it must be remembered that our knowledge of most of the glycols is extremely deficient, and that it is probable that further inquiry will show that many of the statements which have been made are erroneous, a circumstance due to the very small quantities of material operated upon. Only the glycols which are arranged in the table in the *same* vertical series are strictly homologous.

§ VII. DIHYDRIC ALCOHOLS OF THE $C_nH_{2n-8}(OH)_2$ SERIES.

(1505) These are derived from the hydrocarbons of the C_nH_{2n-6} series by the displacement of two atoms of hydrogen by two OH groups, and for the sake of convenience may be divided into three classes: the dihydric phenols or *orcinols*, such as the dioxybenzene, resorcin, $C_6H_4(OH)_2$, in which we suppose the OH groups are both united directly with carbon atoms of the benzene nucleus; the *aromatic glycols*, such as xylene-glycol, $C_6H_4(CH_2.OH)_2$, in which, on the contrary, both the OH groups occur in the side chains; and an intermediate class of alcohols of the saligenin series or *saligenols*, which, like saligenin, $C_6H_4(OH).CH_2(OH)$, contain one OH group in the benzene nucleus and the other in the side chain.

The orcinols bear the same relation to the phenols that the glycols bear to the alcohols of the ethylic series, and differ in properties from the glycols in the same manner that the phenols differ from ethylic alcohol and its homologues. From the constitution of the hydrocarbons of the aromatic series, a comparatively large number of isomeric derivatives of this class may exist theoretically, although, as yet, very little is known about them. Thus, benzene may furnish three isomeric dihydroxyl derivatives in which the OH groups occupy relatively to one another the ortho- or 1 : 2 position, the meta- or 1 : 3 position, and the para- or 1 : 4 position respectively; whilst toluene is capable of yielding two distinct compounds in which the OH groups occupy the ortho-position relatively to one another; three meta-derivatives; and one para-derivative:*

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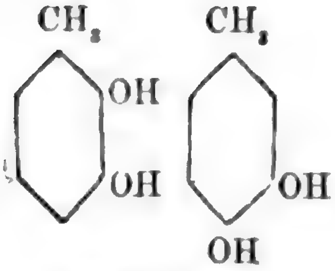
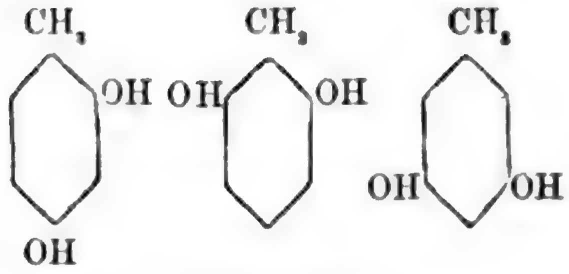
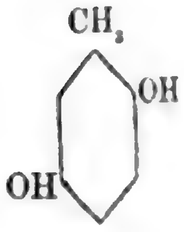
* No systematic nomenclature has been proposed for the ortho-, meta-, and



Ortho-derivatives.



Meta-derivatives.



Para-derivative.

Although many processes have been employed for the preparation of the dihydroxyl derivatives of benzene, scarcely anything is known of the application of these methods to the preparation of their higher homologues. It is possible, however, that the following may be found to be more or less general :

1. Treatment of the ethyl or methyl ethers of the formula $C_nH_{2n-8}(NH_2)(OC_2H_5)$, derived from the monamido-derivatives of the phenols, with nitrous acid, and subsequent conversion of the sulphate of the diazo-compound thus produced into the ethyl compound $C_nH_{2n-8}(OH)(OC_2H_5)$ by boiling it with water. This ethyl derivative may then be transformed into the dihydric alcohol $C_nH_{2n-8}(OH)_2$ or orcinol by heating it with hydriodic acid, the C_2H_5 group being displaced by hydrogen.

2. From the corresponding hydrocarbons by converting them into disulphonic acids, and fusing the potassic salts of these acids with potassic hydrate.

$$C_nH_{2n-6} + 2H_2SO_4 = C_nH_{2n-8}(HSO_3)_2 + 2OH_2.$$

$$\underset{\text{Benzene.}}{C_6H_6} + 2H_2SO_4 = \underset{\text{Benzenedisulphonic acid.}}{C_6H_4(HSO_3)_2} + 2OH_2.$$

$$C_nH_{2n-8}(KSO_3)_2 + 2KHO = C_nH_{2n-8}(OH)_2 + 2K_2SO_3.$$

$$\underset{\text{Potassic benzenedisulphonate.}}{C_6H_4(KSO_3)_2} + 2KHO = \underset{\text{Dihydroxyl-benzene.}}{C_6H_4(OH)_2} + 2K_2SO_3.$$

3. From the phenolmonosulphonic acids of the formula $C_nH_{2n-8}(OH)(HSO_3)$, or from the haloid monosulphonic acids $C_nH_{2n-8}X(HSO_3)$, obtained from the monohaloid derivatives of the hydrocarbons of the benzene series by similar treatment.

4. Also from the monohaloid derivatives of the phenols by fusion with potassic or sodic hydrate (comp. Resorcin).

The aromatic glycols closely resemble the alcohols of the benzylic series in their general behaviour. They are prepared from

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para-dihydroxyl derivatives of benzene and its homologues, of which pyrocatechin, resorcin, and hydroquinone may be taken as the types. Considering their analogy to phenol, these three parallel series might be appropriately designated *catechols*, *resorcinols*, and *quinols*.—Eds.

the dihaloid derivatives of the hydrocarbons of the benzene series containing the halogen in the side chains, in the same manner that the alcohols of the benzylic series are prepared from the corresponding monohaloid derivatives; thus:

$$\underset{\text{Xylylic chloride.}}{C_6H_4(CH_2Cl)_2} + 2KC_2H_3O_2 = \underset{\text{Xylylic acetate.}}{C_6H_4(CH_2.C_2H_3O_2)_2} + 2KCl;$$

$$\underset{\text{Xylylic acetate.}}{C_6H_4(CH_2.C_2H_3O_2)_2} + 2KHO = \underset{\text{Xylene-glycol.}}{C_6H_4(CH_2.OH)_2} + 2KC_2H_3O_2.$$

All the aromatic glycols at present known contain the OH groups in different side chains.

No general methods for the preparation of the saligenols have been devised.

(1506) DIHYDROXYL DERIVATIVES OF BENZENE.—The three possible dihydroxyl derivatives of benzene are all known—namely, pyrocatechin, resorcin, and hydroquinone, which are the ortho-, meta-, and para-compounds respectively. Of these, resorcin resembles phenol far more closely in its chemical properties than either of the other two.

(1507) RESORCIN or *Resorcinol; Metadioxybenzene:* $C_6H_4(OH)_2$.—Resorcin, although a meta-compound, is often obtained from both meta- and para-di-derivatives of benzene by fusion with potassic hydrate. For instance, on treating *meta*bromophenol from metanitraniline in this manner, it is converted into resorcin (Wurster and Nölting, *Deut. chem. Ges. Ber.*, vii. 904); and according to Fittig and Mager (*ibid.*, vii. 1177), *para*bromophenol under similar circumstances yields resorcin without a trace of hydroquinone. It has also been prepared by a similar process from parachloro-, parabromo-, and pariodobenzenesulphonic acids, and from both benzenemeta- and benzeneparadisulphonic acids (Barth and Senhofer, *ibid.*, viii. 1483); in fact, probably the best method of preparing resorcin is to convert the mixture of the two last mentioned acids, which is formed on heating benzene with fuming sulphuric acid, into potassic salts, and to fuse the mixture of potassic salts with potassic hydrate. Pariodphenol, when fused with potassic hydrate at a high temperature, yields nothing but resorcin (Nölting and Wrzcsinski, *ibid.*, viii. 820), although, according to Körner (*Ann. Chem. Pharm.*, cxxxvii. 216), at 165° (329° F.) it yields nothing but hydroquinone. Resorcin may also be obtained from parachlorophenol (B.P. 218° C.) (Faust, *Deut. chem. Ges. Ber.*, vi. 1022). It would appear, in fact, that isomeric change almost invariably takes place when the para-derivatives of benzene are fused with potassic hydrate, resorcin being formed in place of hydroquinone; no similar change has yet been observed in the case of the ortho-derivatives, however. According to Woelz (*Ann. Chem. Pharm.*, clxviii. 91), fused potassic hydrate is without action on hydroquinone; therefore, the supposition that hydroquinone is first produced, and subsequently undergoes isomeric change owing to an action of the potassic hydrate, is not admissible: apparently, the change takes place at the very moment at which the hydroquinone is formed. Resorcin is also formed when galbanum, assafœtida, ammoniacum, sagapenum, or acaroïd resins are fused with potassic hydrate; it was, in fact, whilst studying the action of the alkalies on galbanum that Hlasiwetz and Barth discovered this interesting compound (*Ann. Chem. Pharm.*, cxxx. 354); umbelliferone, $C_9H_6O_3$, and brazilin, $C_{22}H_{18}O_7$, also yield resorcin when similarly treated.

In all these cases the substance to be operated on is heated with two or three times its weight of potassic or sodic hydrate until the mass is in a state of tranquil fusion. It is then poured out on a stone or metal surface, the cake dissolved in a small quantity of water, and the solution strongly acidulated with dilute sulphuric acid. After allowing the mixture to stand for twenty-four hours, the liquid is separated from the crystals of sodic or potassic sulphate, filtered, and agitated with ether to which from 5 to 10 per cent. of alcohol has been added; this takes up the resorcin, which is obtained in the crystalline state on separating the ethereal layer and distilling off the ether. It may be purified by distillation and crystallization from benzene. Kopp considers one of the best processes for preparing resorcin to be the dry distillation of the impure brazilin cake formed on adding calcic carbonate to the wash waters obtained in the manufacture of brazilin from Brazil wood extract, and evaporating to dryness (*Deut. chem. Ges. Ber.*, vi. 446).

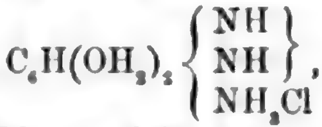
Resorcin crystallizes in colourless triclinic or orthorhombic prisms, which are easily soluble in water, and excessively so in alcohol or ether. It melts at 110° (230 F.), and boils at about 270° (518° F.). No metallic derivatives of resorcin are known. Oxidizing agents act violently on resorcin, forming oxalic acid; nitric acid, however, gives rise at the same time to a small quantity of trinitroresorcin or styphnic acid. Its aqueous solution is coloured dark violet by ferric chloride; the addition of ammonia decolorizes the liquid.

(1508) *Haloid Derivatives of Resorcin.*—When chlorine is passed into an aqueous solution of resorcin, brown amorphous products are produced, but if a concentrated solution of resorcin be added to 'chlorine hydrate' (335), taking care to keep the latter in excess, a crystalline '*pentachlororesorcin*,' $C_6HCl_5O_2$, is obtained. It may be more conveniently prepared by adding alternately in small portions 5 parts of potassic chlorate and a solution of 2 parts of resorcin in 8 of hydrochloric acid to 40 parts of hydrochloric acid, always keeping the chlorate in excess and cooling the mixture. It may be purified by crystallization from carbonic bisulphide, and forms colourless plates or prisms, which melt at 92°·5 (198°·5 F.), easily soluble in alcohol or ether; when treated with hydriodic acid it yields a crystalline *trichlororesorcin* (Stenhouse, *Ann. Chem Pharm.*, clxiii. 182).

The action of excess of bromine on resorcin gives rise to the so-called *pentabromoresorcin*, $C_6HBr_5O_2$, a compound almost insoluble in water, but easily soluble in alcohol or ether; it melts at 113°·5 (236° 3 F.), and like the chlorinated compound is converted into *tribromoresorcin* by the action of hydriodic acid (Stenhouse, *loc. cit.*). Liebermann and Dittler (*ibid.*, clxix. 252) have found that 'pentabromoresorcin,' when carefully heated to about 150° (302° F.), loses a molecule of bromine, and becomes converted into *tribromoresorquinone*, $C_6HBr_3O_2$, a yellow crystalline substance. *Iodoresorcin*, $C_6H_5IO_2$, is a colourless crystalline substance formed by the action of iodine, in presence of lead oxide, on resorcin in ethereal solution. According to Hlasiwetz, aqueous solutions o resorcin, in common with those of orcin and phloroglucin, are capable of dissolving a considerable quantity of iodine without acquiring a distinct yellow colour. The iodine cannot be detected in these solutions by the ordinary reagents, neither is it volatilized by boiling them; on evaporating the liquid in vacuo, however, the resorcin crystallizes out unchanged, whilst the iodine sublimes.

(1509) *Nitroso- and Nitro-derivatives of Resorcin.*—Resorcin is readily converted into *dinitrosoresorcin*, $C_6H_2(NO)_2(OH)_2$, by the action of nitrous acid on its aqueous solution; the mono-potassium derivative of this compound separating shortly after the addition of a solution of potassic nitrite to a solution of resorcin acidified with acetic acid. Dinitrosoresorcin crystallizes in glistening yellowish-brown plates, containing two molecules of water of crystallization; it furnishes two series of metallic derivatives, the mono-derivatives being difficultly soluble, but the di-derivatives easily soluble in water; nitric acid, even if very dilute, converts it into trinitroresorcin, and it is entirely decomposed on oxidation by potassic permanganate or ferricyanide; it is readily reduced, however, to diamidoresorcin (Fitz, *Deut. chem. Ges. Ber.*, viii. 631).

Monitroresorcin: $C_6H_3(NO_2)(OH)_2$, is formed along with diazoresorcin* by the action of nitrous acid on resorcin in ethereal solution, and is extracted from the mother liquors. It crystallizes in long yellow needles, which melt at 115° (239° F.). It forms two series of metallic derivatives, in which one or both of the hydrogen atoms in the hydroxyl groups are displaced; they crystallize well, and are of a yellow or orange-red colour. On reduction it yields amidoresorcin; and by the action of bromine, it is converted into dibromonitroresorcin, which crystallizes in yellow plates melting at 147° (296°·6 F.) (Weselsky, *Ann. Chem. Pharm.*, clxiv. 1).

Trinitroresorcin, styphnic or *oxypicric acid:* $C_6H(NO_2)_3(OH)_2$, may be prepared directly from resorcin by adding a concentrated solution to well cooled fuming nitric acid, and subsequently dropping the mixture into sulphuric acid cooled to − 15° (5° F.). On pouring the product into water, the nitro-derivative separates as a crystalline powder, which may be purified by crystallization from hot water (Stenhouse, *Proc. Roy. Soc.*, xix. 410). It is also formed by the action of nitric acid on brazilin, or on the extracts of Brazil wood or Sapan wood, and from euxanthone, euxanthic acid, or peucedanin. Assafœtida, ammoniacum, galbanum, or sagapenum, and in all probability all resins which yield resorcin when fused with potassic hydrate, give trinitroresorcin when treated with nitric acid Trinitroresorcin crystallizes in pale yellow laminæ, or hexagonal prisms, which melt at 175°·5 (347°·9 F.); like trinitrophenol, it readily furnishes metallic derivatives. On reduction it is converted into triamidoresorcin, $C_6H(NH_2)_3(OH)_2$, the hydrochloride of which furnishes diimidoamidoresorcin hydrochloride,  $C_6H(OH_2)_2\left\{\begin{array}{l}NH\\NH\\NH_2Cl\end{array}\right.$, on treatment with ferric chloride (Schreder, *Ann. Chem. Pharm.*, clviii. 244).

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* The chief product of the action of nitrous acid on an *ethereal* solution of resorcin is the so-called *diazoresorcin*, $C_{18}H_{12}N_2O_6 = 3C_6H_6O_2 + 2HNO_2 - 4H_2O$. It is remarkable that phenol and resorcin both yield nitroso-derivatives when submitted to the action of nitrous acid in *aqueous* solution, but diazo-derivatives when the action takes place in an ethereal solution; this subject will be further discussed under diazo-compounds. Orcin yields a body of the composition $C_{14}H_{11}NO_3 = 2C_7H_8O_2 + HNO_2 - 3OH_2$, when its ethereal solution is treated with nitrous acid.

(1510) PYROCATECHIN or *Catechol; Orthodioxybenzene*: $C_6H_4(OH)_2$.—This compound derives its name from the fact that it was originally obtained by the dry distillation of catechu: kino, moritannic acid, and all the various species of tannin which give a green coloration with ferric selts, also yield pyrocatechin when submitted to similar treatment. Protocatechuic acid, $C_6H_3(OH)_2.COOH$—which bears the same relation to pyrocatechin that salicylic acid does to phenol—when heated, splits up into pyrocatechin and carbonic anhydride; and generally those compounds which yield protocatechuic acid when fused with potassic hydrate give pyrocatechin when submitted to destructive distillation. Pyrocatechin has also been obtained in small quantity by fusing orthochlorophenol, orthiodophenol, and phenolorthosulphonic acid with potassic hydrate. It is most readily prepared by passing gaseous hydriodic acid into guaiacol, $C_6H_4(OH)(OCH_3)$, which is heated in a retort to 195°—200° (383°—392° F.), as long as methylic iodide is produced; the pyrocatechin is separated from the residue by fractional distillation, and purified by crystallization from benzene (Baeyer, *Deut. chem. Ges. Ber.*, viii. 153).

Pyrocatechin forms colourless, shining laminæ, belonging to the trimetric system. It melts at 102° (215°·6 F.) (Fittig and Remsen; Tiemann, *ibid.*, viii. 510), but begins to volatilize at a much lower temperature; its boiling point is variously stated, but appears to be about 245° (473° F.). It is very readily soluble in water and in alcohol, but less so in benzene, the latter solvent affording an excellent means of purifying it. It is violently acted on by nitric acid, being oxidized to oxalic acid. Its solutions are coloured dark green by ferric chloride, the colour being changed by alkalies to a deep red. On adding plumbic acetate to a solution of pyrocatechin, a white precipitate of the compound $C_6H_4O_2Pb$ is produced; by this reaction, and by the coloration with ferric chloride, pyrocatechin is readily distinguished from resorcin and hydroquinone.

At present no chloro- or nitro-derivatives of pyrocatechin are known, but a crystalline tetrabromo-derivative, $C_6Br_4(OH)_2$, has been obtained by the action of bromine on pyrocatechin and by heating protocatechuic acid with bromine to 100° (212° F.). Dry bromine is without action on tetrabromopyrocatechin, but on gently warming it with bromine and water a compound of the composition $C_{18}H_2Br_{10}O$ is produced, which crystallizes in dark crimson coloured plates (Stenhouse, *Journ. Chem. Soc.*, xxviii. 6).

(1511) HYDROQUINONE or *Quinol; Paradioxybenzene:* $C_6H_4(OH)_2$.—This compound is usually prepared by the action of nascent hydrogen on quinone, $C_6H_4O_2$—by treating the latter with an aqueous solution of sulphurous or hydriodic acid, or with tin and hydrochloric acid. It is the chief product of the destructive distillation of quinic acid, and of the dioxybenzoic acid termed gentisic acid, oxysalicylic acid, or hydroquinone-carboxylic acid (Hlasiwetz and Habermann, *Ann. Chem. Pharm.*, clxxx. 343; Demole, *Deut. chem. Ges. Ber.*, vii. 1441; Rakowsky and Leppert, *ibid.*, viii. 788).

It may be produced from paranitrophenol (M.P. 114° C.) by Griess's method (Salkowski, *ibid.*, vii. 1008), and from pariodophenol by fusion with potassic hydrate (Körner); it may also be prepared from phenol in the following manner:

Phenol is first converted into diazophenol by passing nitrous vapours into a well cooled ethereal solution; after some time the liquid becomes filled with needles of diazophenol nitrate, $C_6H_4(OH).N_2(NO_3)$, which are dissolved in a suitable quantity of dilute sulphuric acid (1 vol. H_2SO_4 to 2 vols. water), the solution mixed with alcohol, and sufficient ether then added to cause turbidity. The diazophenol sulphate, which after some time crystallizes from the well cooled solution, is dissolved in water, the solution mixed with 10 to 15 per cent. of concentrated sulphuric acid, and then heated until the liquid assumes a dark red colour; the hydroquinone thus produced is extracted by agitating the cold solution with ether (Weselsky, *ibid.*, viii. 98; ix. 1059).

Hydroquinone forms transparent colourless rhombic plates or prisms, which melt at 169° (336°·2 F.) (Hlasiwetz, *loc. cit.*), and sublimes readily in glistening plates. It is easily soluble in hot water and also in alcohol or ether. It dissolves in an aqueous solution of the alkaline sulphites, and is readily converted by the action of ferric chloride and of oxidizing agents generally, first into the so-called quinhydrone, and subsequently into quinone, $C_6H_4O_2$. Hydroquinone and resorcin both yield sulpho-acids which require investigation.

(1512) *Haloid Derivatives of Hydroquinone.*—These cannot be obtained directly from hydroquinone, as the first action of the halogen is to remove hydrogen and convert it into quinone: $C_6H_4(OH)_2 + Cl_2 = C_6H_4O_2 + 2HCl$, which by the further action of the halogen yields haloid derivatives of quinone. In all cases the haloid derivatives of hydroquinones are obtained by the action of reducing agents on the corresponding haloid quinone derivatives; they are all colourless. *Monochlorhydroquinone*, $C_6H_3Cl(OH)_2$, is readily soluble in water and very soluble in alcohol or ether. *Dichlorhydroquinone*, $C_6H_2Cl_2(OH)_2$, forms nacreous crystals which melt at 164° (327°·2 F.), but begin to sublime at 120° (248° F.); it is only sparingly soluble in cold water, but readily soluble in alcohol or ether. *Trichlorhydroquinone*, $C_6HCl_3(OH)_2$, crystallizes in plates, which melt at 134° (273°·2 F.) and sublime readily; it is only moderately soluble in boiling water. *Tetrachlorhydroquinone* or *chlorhydranil*, $C_6Cl_4(OH)_2$, is insoluble in water. These four chlorinated derivatives offer a very good example of the graduated change in physical properties produced by the successive displacement of the hydrogen atoms in a compound by halogens. As the amount of chlorine increases the solubility and volatility of the compound decreases, until in the case of tetrachlorhydroquinone, where all the hydrogen atoms directly united with carbon are displaced, the substance becomes insoluble in water, and cannot be volatilized without decomposition under the ordinary pressure. *Tribromhydroquinone*, $C_6H_2Br_3(OH)_2$, and *tetrabromhydroquinone* or *bromhydranil*, $C_6Br_4(OH)_2$, are colourless crystalline substances closely resembling the corresponding chlorinated derivatives in appearance and properties. No iodine derivatives are known. Strecker obtained a dinitrohydroquinone together with glucose, by heating dinitroarbutin with very dilute sulphuric acid:

$$C_{12}H_{14}(NO_2)_2(OH)_2 + OH_2 = C_6H_2(NO_2)_2(OH)_2 + C_6H_{12}O_6.$$

It crystallizes in golden yellow glistening plates.

(1513) *Constitution of the Dihydroxyl Derivatives of Benzene.*—Not only has the constitution of these compounds been the subject of much discussion, but the views now entertained with regard to them are very different from those formerly held by chemists. Thus, resorcin, which we now regard as metadioxybenzene, was long supposed to be a para-di-derivative of benzene, owing to the fact that a number of compounds from which it was obtained on fusion with potassic hydrate, when distilled with potassic cyanide, were converted into a dicyanobenzene capable of yielding an undoubted para-di-derivative—namely, terephthalic acid: the occurrence of isomeric change, especially in the case of compounds which theoretically should furnish hydroquinone, being unsuspected. At that time hydroquinone was placed in the ortho- and not, as at present, in the para-series of di-derivatives, on account of its relation to quinone, which Graebe regarded as formed from benzene by the displacement of two *contiguous* hydrogen atoms by the dyad group $(O-O)''$, although, as will be shown later on, the reasons for this conclusion were of the most artificial character.

As the considerations upon which our views of the constitution of the di-derivatives of benzene, and of the phenol derivatives, are based have already been discussed at length, it will only be necessary to point out that the constitution of hydroquinone is established by its formation from paranitrophenol and from pariodophenol, and especially by its relation to quinone (q.v.); the constitution of pyrocatechin being determined by its formation from orthochlorophenol (from orthonitrophenol) and orthiodophenol on fusion with potassic hydrate. Hydroquinone being para-, and pyrocatechin orthodioxybenzene, it follows that resorcin is metadioxybenzene; but the superior stability of resorcin, as compared with its isomerides, alone almost justifies our placing it in the meta-series, the meta-di-derivatives of benzene, to judge from all recent investigations, being as a class of much greater stability than the ortho- or para-derivatives.

(1514) Dihydroxyl derivatives of Toluene: $C_7H_6(OH)_2=124$.—Our knowledge of these compounds is extremely limited, only two having been investigated—namely, saligenin, $C_6H_4(OH).CH_2(OH)$, and orcin, $CH_3.C_6H_3(OH)_2$; a number of isomerides of orcin have been obtained, but only imperfectly described.

(1515) Saligenin or *Saligenol:* $C_6H_4(OH).CH_2(OH)$; *Orthomethoxyphenol:* $(OH : CH_2.OH=1 : 2)$.—This compound partakes both of the character of a phenol and of a primary alcohol, and is formed by the action of nascent hydrogen on salicylic or orthoxybenzoic aldehyde, $C_6H_4(OH).COH$, on treating the latter with sodium amalgam in presence of water. It is, however, most conveniently prepared from salicin, $C_{13}H_{18}O_7$, the glucoside of saligenin, by decomposing it with emulsin or synaptase, or by boiling it with dilute acid, as recommended by Piria, the reaction which takes place being represented by the equation:

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + OH_2 = \underset{\text{Saligenin.}}{C_7H_8O_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

The saligenin is extracted from the aqueous solution by agitating it with ether, and separates on evaporating the ethereal solution. It crystallizes in colourless rhombic plates which melt at 82° (179° F.), and sublimes at 100° (212° F.). It is excessively soluble in boiling water, and in alcohol or ether; it also dissolves easily in hot benzene. One of its most characteristic reactions is the bright indigo-blue coloration which its aqueous solution gives with ferric salts. It is easily reconverted into salicylic aldehyde by the action of most oxidizing agents, such as chromic acid, argentic oxide, &c., although when oxidized by a mixture of manganic peroxide and sulphuric acid, it gives nothing but formic acid and carbonic anhydride without a trace of the aldehyde.

A *monochlorosaligenin,* $C_7H_5Cl(OH)_2$, and a *dichlorosaligenin,* $C_7H_4Cl_2(OH)_2$, have been obtained from the corresponding chlorosalicins by the action of emulsin. They are both colourless crystalline substances.

(1516) Orcin or *Orcinol;* (?) *Methylresorcinol:* $CH_3.C_6H_4(OH)_2$.—Orcin was discovered in the *Variolaria dealbata* by Robiquet in

1829, who obtained it by treating the lichen with alcohol, evaporating, and exhausting the residue with water; the aqueous solution, when concentrated and allowed to stand, deposited the orcin in a crystalline state. Although small quantities of this compound appear to exist in various lichens, it is invariably obtained by decomposing erythrin or lecanorin by boiling it with calcic hydrate and water. When erythrin is thus treated, the first action which takes place is undoubtedly that represented by the equation:

$$\underset{\text{Erythrin.}}{C_{20}H_{22}O_{10}} + OH_2 = \underset{\text{Picroerythrin.}}{C_{12}H_{16}O_7} + \underset{\text{Orsellinic acid.}}{C_8H_8O_4};$$

the erythrin being decomposed and converted into picroerythrin and orsellinic acid. The orsellinic acid, $CH_3.C_6H_2(OH)_2.COOH$, which bears the same relation to orcin that salicylic acid, $C_6H_4(OH).COOH$, does to phenol, then loses the elements of carbonic anhydride by the further action of the lime, and yields orcin, thus:

$$\underset{\text{Orsellinic acid.}}{C_6H_2(CH_3)(OH)_2.COOH} = \underset{\text{Orcin.}}{C_6H_3(CH_3)(OH)_2} + CO_2.$$

Picroerythrin, a body which may be regarded as an acid ethereal salt of the tetrahydric alcohol erythrite, and as having the composition $C_6H_2(CH_3)(OH)_2.COO(C_4H_9O_3)$, is also readily decomposed by the hydrates of the alkalies and alkaline earths into erythrite and orsellinic acid; but the latter at the instant of its liberation is resolved into orcin and carbonic anhydride:

$$\underset{\text{Picroerythrin.}}{C_{12}H_{16}O_7} + BaH_2O_2 = \underset{\text{Orcin.}}{C_7H_8O_2} + \underset{\text{Erythrite.}}{C_4H_{10}O_4} + BaCO_3.$$

Lecanorin, $C_{16}H_{14}O_7$, which is apparently the anhydride of orsellinic acid, is also resolved into orcin and carbonic anhydride under the influence of alkalies; orsellinic acid, or rather a metallic orsellinate, being formed as an intermediate stage of the reaction:

$$\underset{\text{Lecanorin.}}{\left.\begin{matrix}C_8H_7O_3\\C_8H_7O_3\end{matrix}\right\}O} + OH_2 = \underset{\text{Orsellinic acid.}}{2C_8H_8O_4}.$$

Orcin has also been found by Hlasiwetz (*Ann. Chem. Pharm.*, cxxxiv. 287), together with paroxybenzoic acid, amongst the products of the action of fused potassic hydrate on aloes.

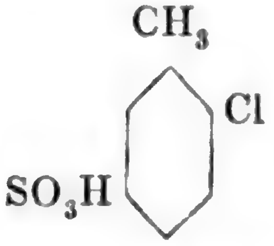
In order to prepare orcin, the freshly precipitated moist lecanorin or erythrin is boiled with water and excess of lime for about half an hour, taking care to avoid access of air as far as possible, which otherwise would cause the formation of a red coloured resinous matter. The solution is filtered, the excess of lime removed by a stream of carbonic anhydride (or more conveniently on a large scale by exactly neutralizing with dilute sulphuric acid), again filtered, and evaporated to dryness on a water bath. The orcin may readily be extracted from this product by exhausting it with a mixture of coal-tar hydrocarbons, boiling at about 110° (230° F.), which dissolves the orcin, but leaves the various dark-coloured impurities, and also the erythrite (the latter, however, is only present when erythrin has been used as the source of the orcin); if the hot solution is agitated with water, the orcin is removed, and the hydrocarbon can be at once poured back on to the residue. The aqueous solutions when sufficiently concentrated yield nearly pure orcin in a crystalline state. The brown coloured residue, after being exhausted by the hydrocarbon, readily yields erythrite by crystallization from boiling water. It is easier, however, when very large quantities of substance are operated upon, to dissolve out the orcin by treating the solid product with alcohol, and subsequently to purify it by repeated crystallizations from hot water.

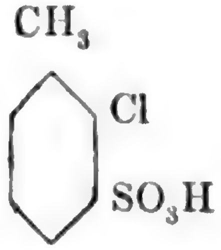
As thus obtained it forms hexagonal monoclinic prisms, containing a molecule of water of crystallization, and having therefore the composition $C_7H_8O_2 + OH_2$; when pure it is colourless, but on exposure to the air it soon becomes of a pale reddish-brown colour. These crystals fuse at 58° (136°·4 F.) with loss of water; whilst anhydrous orcin melts at 86° (186°·8 F.). At a higher temperature orcin distils, the first portions of the distillate containing some water, whilst subsequently anhydrous orcin passes over at 290° (554° F.); in this operation a slight decomposition takes place if conducted at the ordinary atmospheric pressure, but under diminished pressure it distils as a colourless oil, which solidifies on cooling. In fact, distillation in vacuo forms by far the best method of obtaining pure and colourless orcin.

Orcin is exceedingly soluble in alcohol, ether, or boiling water, but much less soluble in cold water. It is only moderately soluble in boiling benzene. It has a very sweet, but somewhat astringent taste. It has marked acid properties, fused orcin decomposing sodic carbonate with evolution of carbonic anhydride. Like its lower homologues it readily enters into reaction with acid chlorides, forming compounds such as the acetate $CH_3.C_6H_3(O.C_2H_3O)_2$. Oxidizing agents readily attack it with formation of oxalic acid; and like phenol, when heated with concentrated sulphuric acid it gives rise to a sulphonic acid. The two most remarkable and characteristic reactions of orcin, however, are those which take place when it is treated with hypochlorites, and with ammonia. Hypochlorites give an intense, but transient purple red colour with the most minute trace of orcin or any of those lichen acids which yield it; Stenhouse (*Journ. Chem. Soc.*, xx. 221) has founded on this a volumetric process for the determination of the value of "orchella weed." When a solution containing orcin and ammonia is exposed to the air, it rapidly acquires a deep purple colour, that of the so-called orchil or archil so largely used for blooming indigo dyed goods. When potassic or sodic carbonate is present as well as ammonia, a blue colouring matter is formed, identical with that contained in litmus.

(1517) *Constitution of Orcin.*—Vogt and Henninger (*Ann. Chim. Phys.* [4], xxvii. 129), by treating with sulphuric acid the (o–1)chlorotoluene prepared by the action of chlorine on toluene in presence of iodine, obtained a mixture of two chlorotoluenesulphonic acids, $CH_3.C_6H_3Cl.SO_3H$, which were separated by taking advantage of the difference in the solubility of their baric salts. By fusing the potassic salt of the *a*-acid with about twice its weight of potassic hydrate, dissolving the fused mass in water, and extracting the acidified solution with ether in the usual way, an ethereal solution was obtained, which furnished a brown syrup on evaporation of the ether; by distilling this syrup in vacuo, and crystallizing the distillate from water, crystals were obtained of the composition $C_7H_8O_2+OH_2$, having all the properties of the orcin prepared from lichens. The melting point of the synthetic product was found to be 57°·1 (134°·8 F.), and there appears to be but little doubt as to its identity with the natural product.

Now the chlorotoluene employed by Vogt and Henninger was undoubtedly a mixture of the ortho- and para-compound, but from their description of the salts of their *a*-acid, it is evident that the latter is identical with the *ortho*chlorotoluenesulphonic acid of Hübner and Majert (*Deut. chem. Ges. Ber.*, vi. 790); the constitution of this acid has not been directly ascertained, but the investigations carried on under Hübner's direction (*Ann. Chem. Pharm.*, clxix. 1) have shown that orthobromotoluene, the behaviour of which it can scarcely be doubted is strictly comparable with that of orthochlorotoluene, furnishes only a single sulpho-acid, and that the sulpho-group in this acid is in the meta-position relatively to the methyl group of toluene. Only two formulæ are, therefore, possible for orthochlorotoluenesulphonic acid—namely:





As the behaviour of the mono-derivatives of toluene is frequently analogous to that of the corresponding derivatives of benzene, the first of these formulæ is the more probable, since chlorobenzene is converted into parachlorobenzenesulphonic acid on treatment with sulphuric acid. From this it might appear as if the hydroxyl groups in orcin occupied the same relative positions as in hydroquinone, $CH_3 : OH : OH = 1 : 2 : 5$; but since the reactions and properties of orcin and resorcin so very closely resemble one another, it is highly probable that, as in the formation of resorcin from parachlorobenzenesulphonic acid, an isomeric change takes place during the fusion with potassic hydrate, and that the orcin produced in the reaction is really methylmetadioxybenzene, $CH_3 : OH : OH : 1 : 2 : 4$.

(1518) *Haloid and Nitro-derivatives of Orcin.*—When chlorine is passed into an aqueous solution of orcin, or when dry orcin is treated with the gas, dark brown resinous products are produced, from which no well-defined crystalline product has been obtained. When, however, an aqueous solution of orcin is added to the so-called 'chlorine hydrate,' or to a mixture of hydrochloric acid with potassic chlorate, care being taken to keep the chlorinating agent in excess, a colourless crystalline product is obtained, which may be readily purified by crystallization from carbonic bisulphide. It melts at 120°·5 (248°·9 F.), and has the composition of *pentachlororcin*, $C_7H_3Cl_5O_2$. From Liebermann and Dittler's investigation of the so-called pentabromoresorcin (p. 523), it is highly probable, however, that this substance is not merely a chlorine substitution derivative of orcin, $C_7HCl_5(OH)_2$, but a chlorine additive compound, $C_7H_3Cl_3O_2.Cl_2$, partaking of the nature of a quinone. It is a curious circumstance that the compound $C_7H_3Cl_5O_2$ is capable of uniting directly with a molecule of hypochlorous acid when it is treated with a solution of an hypochlorite to which hydrochloric acid has been added. The compound, $C_7H_3Cl_5O_2.HClO$, is also obtained when orcin dissolved in hydrochloric acid is added to a solution of bleaching powder. When "pentachlororcin" is treated with a reducing agent, such as hydriodic acid, two of the chlorine atoms are displaced by hydrogen, and *trichlororcin*, $C_7H_3Cl_3(OH)_2$, is produced. It forms colourless needles, which melt at 123° (253°·4 F.).

"*Pentabromorcin,*" $C_7H_3Br_5O_2$, is readily formed on adding an aqueous solution of orcin, with constant agitation, to a mixture of bromine and water. It crystallizes in large colourless prisms, which melt at 126° (258°·8 F.): treatment with dilute hydriodic acid converts it into tribromorcin, $C_7H_3Br_3(OH)_2$ (Lamparter, *ibid.*, cxxxiv. 257; Stenhouse, *Proc. Roy. Soc.*, xx. 72). A *monobromorcin*, $C_7H_5Br(OH)_2$, was obtained by Lamparter, on mixing solutions containing molecular weights of bromine and orcin and evaporating. A *triodorcin*, $C_7H_3I_3(OH)_2$, crystallizing from carbonic bisulphide in large transparent plates, is produced when an aqueous solution of orcin is precipitated with a solution of iodine monochloride; and a *moniodorcin*, $C_7H_5I(OH)_2$, has been obtained by treating an ethereal solution of orcin and iodine with finely powdered lead oxide (Stenhouse, *ibid.*, xxii. 53).

Nitro-derivatives of Orcin.—According to Weselsky (*Deut. chem. Ges. Ber.*, vii. 439), when an ethereal solution of orcin is treated with a solution of nitrous in nitric acid, two isomeric *mononitroorcins*, $C_7H_5(NO_2)(OH)_2$, are produced, together with other compounds, and are obtained on evaporating the clear ethereal solution. The *α-nitroorcin* being volatile in the vapour of water, is readily separated. It crystallizes in long orange-red needles, which melt at 120° (248° F.), and are easily soluble in alcohol or ether, but only sparingly in cold water. The *β-nitroorcin* obtained from the tarry residue by boiling it with water, forms short lemon-yellow needles, which melt at 115° (239° F.); on adding bromine to its ethereal solution, *dibromo-β-nitroorcin*, $C_7H_3Br_2(NO_2)(OH)_2$, is obtained in dark yellow plates melting at 112° (233°·6 F.). *Trinitroorcin*, $C_7H_3(NO_2)_3(OH)_2$, is prepared from orcin by dissolving it in a small quantity of warm water, and adding the solution gradually to fuming nitric acid which has been cooled to − 16° (5° F.) by a freezing mixture. The pale brown solution thus obtained is then slowly added to about twice its bulk of concentrated sulphuric acid also cooled to the same temperature; after about twenty minutes the resulting pasty mass is poured into a mixture of crushed ice and water, and the bright yellow precipitate, after being washed and dried, is recrystallized from boiling water. It forms large yellow needles, soluble in alcohol, ether, and benzene, which fuse at 162° (323°·6 F.), and at a slightly higher temperature decompose with a feeble explosion; although it resembles trinitrophenol in dyeing the skin yellow, it has not the slightest bitter taste (Stenhouse, *Proc. Roy. Soc.*, xix. 410). The nitroorcins furnish a number of crystalline orange-yellow or red metallic derivatives, such as potassium trinitroorcin, $CH_3.C_6(NO_2)_3(OK)_2$.

(1519) *Isomerides of Orcin.*—A crystalline compound apparently isomeric with orcin has been obtained by Senhofer (*Ann. Chem. Pharm.*, clxiv. 131) by fusing the potassic salt of the toluenedisulphonic acid prepared by heating toluene with sulphuric acid and phosphoric anhydride to 230° (446° F.) for four or five hours with an excess of potassic hydrate, &c. It crystallizes in fine needles containing a molecule of water; the anhydrous substance melts at 87° (188°·6 F.), and boils at about 260° (500° F.); it gives a brownish-green colour with ferric salts, and when exposed to the air in contact with ammonia forms a brownish solution different from the intense violet-red so characteristic of orcin.

Hakansson (*Deut. chem. Ges. Ber.*, v. 1084), by heating toluenemonosulphonic acid (? the crude acid from toluene and sulphuric acid) with fuming sulphuric acid at 160° (320° F.), found that two disulphonic acids were produced, both of which were distinct from that obtained by Senhofer. The potassic salt of the *a*-acid—that formed in largest quantity by this process—when fused with potassic hydrate yields, besides salicylic acid, a crystalline substance, $C_7H_8O_2$, isomeric with ordinary orcin, and with Senhofer's isoorcin. Like the latter, it forms needles containing water of crystallization, which melt at about 95°; the anhydrous substance melts at 87°—88° (188°·6—190°·4 F.), and boils at about 270° (518° F.). Its most characteristic reactions are, that it gives a yellow colour with calcium hypochlorite, and in contact with air and ammonia, a blue colour, which is changed to red on the addition of acetic acid.

Homopyrocatechin or *Methylcatechol*: $CH_3.C_6H_3(OH)_2$.—Hugo Müller (*Zeits. Chem.*, 1864, 703; *Chem. News*, x. 269), by submitting that portion of English wood creasote which boils at 219° (426°·2 F.) to the action of hydriodic acid, obtained methylic iodide and a syrupy uncrystallizable liquid, soluble in water and capable of being distilled without decomposition. The same substance has since been separated by Gorup-Besanez (*Zeits. Chem.*, 1868, 393) from Rhenish beech tar, and also by Marasse (*Ann. Chem. Pharm.*, clii. 75), along with phlorol, cresol, and pyrocatechin, by acting with hydriodic acid on the fraction of beech wood creasote, which boils between 217° and 221° (422°·6 and 428° F.). This body, to which the name homopyrocatechin has been given, is formed from the creosol—the homologue of guaiacol—present in these substances, in the following manner:

$$\underset{\text{Creosol.}}{CH_3.C_6H_3(OH)(OCH_3)} + HI = \underset{\text{Methylcatechol.}}{CH_3.C_6H_3(OH)_2} + \underset{\text{Iodomethane.}}{CH_3I}$$

Homopyrocatechin has not yet been carefully examined, and as the material from which it was prepared does not appear to have been pure creosol, it is doubtful whether the substance itself has ever been obtained in the pure state.

Toluhydroquinone.—Although neither toluquinone, $C_6H_3(CH_3)O_2$, nor toluhydroquinone, $C_6H_3(CH_3)(OH)_2$, is known, a trichlorinated derivative of the latter is obtained from trichlortoluquinone by the action of an aqueous solution of sulphurous acid. *Trichlorotoluhydroquinone* or *trichloromethylquinol*, $C_6Cl_3(CH_3)(OH)_2$, forms colourless needles which melt at 212° (413°·6 F.), and are sparingly soluble in water, but readily in alcohol. It may be sublimed without decomposition.

(1520) Alcohols of the Composition $C_8H_{10}(OH)_2 = 138$.—Xyleneglycol and two compounds of the orcinol class are the only alcohols of this composition which have been obtained.

Xyleneglycol or *Paradimethoxybenzene*: $C_6H_4(CH_2.HO)_2$.—This compound, which bears the same relation to benzylic alcohol, $C_6H_5.CH_2(OH)$, that glycol does to ethylic alcohol, is prepared by heating dichloro- or dibromoparaxylene (p. 321) with thirty times its weight of water at 180° (356° F.), and after concentrating and neutralizing the aqueous solution, extracting the glycol with ether: $C_6H_4(CH_2Cl)_2 + 2OH_2 = C_6H_4(CH_2.OH)_2 + 2HCl$. It crystallizes in glistening needles, readily soluble in water, alcohol, and ether; it melts at 113° (235°·4 F.). On oxidation, it is converted into terephthalic acid (Grimaux, *Compt. Rend.*, lxx. 1363).

Hydrophlorone; (?) Dimethylquinol: $(CH_3)_2C_6H_2(OH)_2$.—This compound is produced when phlorone or dimethylquinone, $C_8H_8O_2$—a substance obtained by the action of sulphuric acid and manganic peroxide on the portion of the coal-tar phenols boiling at 190°—220° (374°—428° F.)—is suspended in water, and a current of sulphurous anhydride passed into the liquid until the crystals have become colourless. It crystallizes from boiling water, in which it is rather soluble, in colourless glistening plates, readily soluble in alcohol or ether. When phlorone is heated with concentrated hydrochloric acid, it dissolves, and *chlorhydrophlorone*, $C_8H_7Cl(OH)_2$, separates on cooling in the crystalline state. When pure it forms colourless silky needles easily soluble in ether, alcohol, or hot water (Rad, *Ann. Chem. Pharm.*, cli. 164).

Betaorcin: (?) $(CH_3)_2C_6H_2(OH_2)$.—This homologue of orcin, which has been very little investigated, was first obtained by Stenhouse (*Ann. Chem. Pharm.*, lxviii. 104) by submitting cladonic acid from *Cladonia rangiferina* to destructive distillation. It has since been prepared by the action of boiling alkaline solutions on *β-erythrin*, a substance homologous with ordinary erythrin obtained from a peculiar variety of *Roccella fuciformis* (Menschutkin, *Bull Soc. Chem.* [2], ii. 424; Lamparter, *Ann. Chem. Pharm.*, cxxxiv. 243).

It crystallizes in brilliant prisms belonging to the dimetric system, which melt at 109° (228°·2 F.), and are less soluble in cold water than orcin; it is easily soluble in alcohol and ether. When treated with nitric and sulphuric acids, as in the preparation of trinitroorcin, betaorcin yields a nitro-derivative. With ammonia it gives a splendid red colour when exposed to the air, and with calcic hypochlorite a blood-red, very different from the purple obtained with orcin.

(1521) Thymohydroquinone or *Methylpropylquinol; thymoïlol*: $C_{10}H_{14}O_2$ or $C_6H_2(CH_3)(C_3H_7)(OH)_2$.—Thymoquinone, a substance obtained from thymolsulphonic acid by distilling it with manganic peroxide and dilute sulphuric acid, when treated with reducing agents is converted into the corresponding hydroquinone. It forms colourless prisms, which fuse at 145° (293° F.) and distil without decomposition at 290° (554° F.). It is only sparingly soluble in water, but readily in alcohol and in ether. Oxidizing agents reconvert it into thymoquinone (Lallemand, *Ann. Chem. Pharm.*, cii. 119; Carstanjen, *Journ. pr. Chem.* [2], iii. 53).

§ VIII. DIHYDRIC ALCOHOLS OF SERIES HIGHER THAN THE $C_nH_{2n-8}(OH)_2$ SERIES.

Very few dihydroxyl derivatives of hydrocarbons containing relatively less hydrogen than those of the benzene series are known, and even those which have been obtained are at present of very little importance.

(1522) HYDRONAPHTHAQUINONE or *Naphthaquinol:* $C_{10}H_8O_2$ or $C_{10}H_6(OH)_2$.—This compound, which is analogous in its properties to hydroquinone or quinol, is prepared by the action of reducing agents such as hydriodic acid or stannous chloride on naphthaquinone. It crystallizes in colourless needles, which melt at 176° (348°·8 F.); it is comparatively soluble in boiling water, but crystallizes out almost entirely on cooling; it is readily soluble in alcohol or ether; oxidizing agents reconvert it into the quinone (Groves, *Journ. Chem. Soc.*, xxvi. 209). Haloid derivatives of naphthaquinol are not known, but they would undoubtedly be obtained by proper treatment from the chloronaphthaquinones.

(1523) DIHYDRIC ALCOHOLS DERIVED FROM THE HYDROCARBONS OF THE DIPHENYL SERIES.—The following are comprised in this series:

			M.P. °C.
Paradiphenol . . .	$HO.C_6H_4.C_6H_4.OH$	...	157°
Orthodiphenol . . .			—
Hydrobenzoin . . .	(?) $C_6H_5.CH(OH).CH(OH).C_6H_5$	...	134
Isohydrobenzoin . .	(?) $C_6H_5.C(OH)_2.CH_2.C_6H_5$	...	120
Dithymol	$C_6H_2(CH_3)(C_3H_7).OH$ | $C_6H_2(CH_3)(C_3H_7).OH$	...	162

(1524) DIPHENOLS: $C_{12}H_8(OH)_2$.—*Paradiphenol* is formed from diparamidodiphenyl or benzidine by Griess's method, and by fusing the sodium salt of phenol*para*sulphonic acid (p. 478) with sodic hydrate, &c. (Lincke, *Journ. pr. Chem.* [2], viii. 43). It crystallizes in fine needles, or small rhombic prisms, which melt at 157° (314°·6 F.); it is difficultly soluble even in boiling water, but readily dissolves in alcohol or ether, and in solutions of the alkalies. It is not reduced when passed over heated zinc dust; it forms substitution derivatives when submitted to the action of bromine, nitric acid, or sulphuric acid (Lincke).

Barth (*Ann. Chem. Pharm.*, clvi. 98) has obtained an isomeric body, together with oxybenzoic and salicylic acids, by fusing phenol with an excess of potassic hydrate until the mass assumed the consistence of a thick syrup, the amount formed being equal to 12—15 per cent. of the phenol employed. It appears to crystallize with difficulty, and does not furnish well characterized substitution derivatives; its aqueous solution is coloured violet by ferric salts. By heating its potassium derivative with methylic iodide it is converted into the dianisol $C_{12}H_8(OCH_3)_2$, which forms octahedral crystals, melting at 146° (294°·8 F.). Judging from its properties, and as it is the tendency of phenol to form ortho- or para-derivatives, it is probable that the compound obtained by Barth is the ortho-modification of diphenol.

According to Goldstein (*Deut. chem. Ges. Ber.*, vii. 734), orthonitrophenol is converted into a dinitrodiphenol on oxidation with potassic permanganate; it sublimes at 150° (302° F.), without fusing, in yellow needles, and dissolves readily in alkalies, forming blood-red coloured solutions. It is probably a derivative of paradiphenol.

(1525) **Hydrobenzoin and Isohydrobenzoin** : $C_{14}H_{12}(OH)_2$.—These compounds are both formed by the action of nascent hydrogen on benzoic aldehyde: $2C_7H_6O + H_2 = C_{14}H_{14}O_2$. When an alcoholic solution of the aldehyde is treated with zinc and hydrochloric acid, hydrobenzoin is the principal product, whilst by the action of sodium amalgam on a solution of the aldehyde in aqueous ether chiefly isohydrobenzoin is formed, but the yield is unsatisfactory in both cases. Hydrobenzoin alone is obtained by the action of nascent hydrogen on benzoin; in fact, the best method of preparing it is to suspend this compound in cold aqueous alcohol, and to add sodium amalgam. Benzil also furnishes only hydrobenzoin when sodium amalgam is added to its warm aqueous solution. Stilbene bromide, $C_{14}H_{12}Br_2$, when heated for some hours to about the boiling point of acetic acid with an equal weight of *argentic* acetate and a small quantity of glacial acetic acid is converted into a mixture of two diacetates of the formula $C_{14}H_{12}(C_2H_3O_2)_2$, which furnish respectively hydrobenzoin and isohydrobenzoin on saponification, a monacetate of the formula $C_{14}H_{12}(OH)(C_2H_3O_2)$ being also formed, which furnishes isohydrobenzoin. But on heating stilbene bromide with *potassic* acetate and acetic acid to about 160°—165° (320°—329° F.) only the di- and monacetate of isohydrobenzoin are obtained, together with an appreciable amount of stilbene. By the action of potassic acetate and alcohol, only stilbene and bromostilbene are produced; argentic benzoate in presence of xylene has an action similar to that of argentic acetate, the dibenzoate of both hydrobenzoin and isohydrobenzoin being formed. Lastly, by the action of argentic oxalate in presence of xylene, resinous products are obtained, together with much stilbene, which on saponification furnish hydrobenzoin almost exclusively (Forst and Zincke, *Ann. Chem. Pharm.*, clxxxii. 241).

Hydrobenzoin crystallizes from alcohol in large, but very thin monoclinic plates; it melts at 134° (273°·2 F.), and is readily soluble in alcohol, but only sparingly in cold water. Its monacetate, $C_{14}H_{12}(OH)(C_2H_3O_2)$, crystallizes in long needles, which melt at 84° (183°·2 F.); the diacetate, $C_{14}H_{12}(C_2H_3O_2)_2$, forms large monoclinic prisms, and melts at 134° (273°·2 F.). The corresponding dibenzoate, $C_{14}H_{12}(C_7H_5O_2)_2$, is one of the most characteristic hydrobenzoin derivatives; it is sparingly soluble in cold ether, alcohol, or benzene, but more soluble in boiling acetic acid, xylene, or alcohol, and crystallizes in small brittle needles, which melt at 247° (476°·6 F). Isohydrobenzoin is readily soluble in alcohol, ether, or chloroform, from which it crystallizes in monoclinic prisms, melting at 119°—120° (246°·2—248° F.); it separates from its aqueous solution in slender glistening needles, containing water of crystallization, which melt at 95°—96° (203°—204°·8 F.) Its monacetate crystallizes in shorter, thicker needles than the isomeride, and melts at 88° (190°·4 F.). The diacetate separates from a hot alcoholic solution in glistening plates, which melt at 117° (242°·6 F.), even after repeated fusion; but it crystallizes from the mother liquor of these crystals on spontaneous evaporation in rhombic prisms, which as a rule melt at 117°—118° (242°·6—244°·4 F.), but after fusion melt constantly at about 106° (232°·8 F.). Sometimes prisms are obtained which from the first melt at 106° (222°·8 F.). On dissolving the crystals which melt constantly at 117° in cold alcohol, and allowing the solution to evaporate spontaneously, prisms are obtained which at first melt at 117°, but afterwards at 106°; it was not found possible to convert the crystals of lower into those of higher melting point (Forst and Zincke). Isohydrobenzoin dibenzoate crystallizes in needles easily soluble in hot alcohol, &c., which melt at 155°—156° (311°—312°·8 F.). On heating isohydrobenzoin with benzoic anhydride to 150°—160° (302°—320° F.), it appears to furnish a *mixture* of the dibenzoates of hydrobenzoin and isohydrobenzoin (Forst and Zincke).

On oxidation with chromic acid, both hydrobenzoin and isohydrobenzoin furnish almost the theoretical amount of benzoic aldehyde and benzoic acid (Forst and Zincke, *Deut. chem. Ges. Ber.*, viii. 799). Nitric acid converts hydrobenzoin into benzoin, $C_6H_5.CO.CH(OH).C_6H_5$; the nature of the crystalline product which is obtained by its action on isohydrobenzoin has not yet been ascertained. Both yield compounds of the composition $C_{14}H_{12}Cl_2$ on treatment with phosphoric pentachloride, but the product from hydrobenzoin is not distinguishable from that from isohydrobenzoin, and both chlorides furnish tolane, $C_6H_5.C{\equiv}C.C_6H_5$, when submitted to the action of potassic hydrate (Amman and Fittig, *Ann. Chem. Pharm.*, clxviii. 67). The brominated compounds $C_{14}H_{12}Br_2$ obtained by the action of phosphorus pentabromide also exhibit the same properties (Forst and Zincke).

The constitution of hydrobenzoin and isohydrobenzoin is involved in considerable obscurity. The formulæ which are most in accordance with their general behaviour are $C_6H_5.CH(OH).CH(OH).C_6H_5$ and $C_6H_5.C(OH)_2.CH_2.C_6H_5$; in fact, their behaviour on oxidation may be regarded as proof that these are the only possible formulæ, since we must suppose that each contains two C_6H_5 groups, the amount of benzoic aldehyde which is formed being almost equal to that required by theory, viz.:

$$C_6H_5.CH(OH).CH(OH).C_6H_5 \ + \ (O + OH_2) \ = \ 2C_6H_5.COH \ + \ 2OH_2.$$

The first formula is the more probable expression of the constitution of hydrobenzoin on account of its formation from benzoin, but many objections may be urged against the second as the formula of isohydrobenzoin. Thus, we may account for the formation of the diacetate $C_6H_5.C(C_2H_3O_2)_2.CH_2.C_6H_5$ from stilbene bromide, which has the formula $C_6H_5.CHBr.CHBr.C_6H_5$, by the action of potassic or argentic acetate in *presence of acetic acid* in the same way that we account for the conversion of isoprimary butylic iodide into tertiary butylic acetate (p. 442)—viz., by the assumption that the stilbene bromide is first converted into bromostilbene, $C_6H_5.CH{=}CBr.C_6H_5$, which then combines with the acetic acid forming the acetate $C_6H_5.CH_2.CBr(C_2H_3O_2).C_6H_5$, which is subsequently converted by double decomposition into the diacetate; but we cannot account in a similar manner for the simultaneous formation of the dibenzoates corresponding to the two alcohols by the action of argentic benzoate on stilbene bromide in presence of the hydrocarbon xylene. Moreover, we have seen that compounds in which two OH groups are associated with the same carbon atom are usually very unstable, and isohydrobenzoin is possessed of considerable stability. Analogy also would lead us to expect that a compound of the formula $C_6H_5.C(OH)_2.CH_2.C_6H_5$ would melt at a lower temperature than the isomeric compound of the formula $C_6H_5.CH(OH).CH(OH).C_6H_5$, whereas hydrobenzoin, to which we have assigned the latter formula, melts at a higher temperature than isohydrobenzoin. The great difference in the properties of the acetates and of the benzoates of hydrobenzoin and isohydrobenzoin does not, however, favour the conclusion that they belong to the class of so-called physical isomerides, but appears rather to indicate that these alcohols are really bodies of different chemical constitution.

(1526) DITHYMOL: $C_{20}H_{24}(OH)_2$.—This compound is the product of the action of ferric chloride on thymol, and crystallizes from dilute alcohol in rhombic plates, containing a molecule of water. It melts at 162° (323°·6 F.); benzoic chloride converts it into the dibenzoate (Boradin and Dianin, *Deut. chem. Ges. Ber.*, viii. 166).

(1527) ANTHRAHYDROQUINONE or *Anthraquinol; dioxyanthracene*: $C_{14}H_8(OH)_2$, is formed when anthraquinone is fused for a long time with potassic hydrate at a temperature superior to 250° (482° F.), but is far more conveniently prepared by pouring a dilute solution of sodic hydrate on a mixture of anthraquinone and zinc dust. The anthraquinone gradually dissolves, and on adding an acid to the solution the anthraquinol is obtained as a yellow precipitate, which rapidly oxidizes in contact with the air, on which account it should be precipitated, washed and dried in an atmosphere of carbonic anhydride (Graebe).

Phenanthrenehydroquinone or *phenanthraquinol:* $C_{14}H_8(OH)_2$, an isomeride of anthraquinol, is obtained in the usual way by the action of sulphurous acid on phenanthraquinone, the action being assisted by a gentle heat. It crystallizes from a hot aqueous solution of sulphurous acid in long colourless needles, which become oxidized in the moist state, but are more stable when dry. The comparative facility with which phenanthrenequinone is converted into the corresponding hydroquinone serves as a means of distinguishing and separating it from anthraquinone, which is not acted on by sulphurous acid (Graebe, *Ann. Chem. Pharm.*, clxvii. 146).

(1528) CHRYSENEHYDROQUINONE or *Chrysenequinol:* $C_{18}H_{10}(OH)_2$.—Pyrenequinone, which is the only known quinone derived from the hydrocarbons of the C_nH_{2n-22} series, has not been converted into the hydroquinone, but chrysenequinone readily yields chrysenehydroquinone: dissolving when boiled with zinc dust in an aqueous solution of potassic hydrate, and on adding an acid to the clear yellow solution the quinol is precipitated in colourless flocks, which readily oxidize. This change takes place even when the quinol is heated to 200° (392° F.) with access of air, the quinone being reproduced, or by dissolving it in sulphuric acid and agitating it with air, when the liquid assumes the blue colour so characteristic of the sulphuric acid solution of chrysenequinone (Liebermann, *ibid.*, clviii. 312).

(1529) DINAPHTHOLS: $C_{20}H_{14}O_2$ or $C_{20}H_{12}(OH)_2$.—On adding ferric chloride (not in excess) to a solution of *a*- or *β*-naphthol, the solution assumes a rose colour, and the corresponding dinaphthol separates in the solid state, the ferric being at the same time reduced to ferrous chloride:

$$\underset{\text{Naphthol.}}{2C_{10}H_7.OH} + Fe_2Cl_6 = \underset{\text{Dinaphthol.}}{C_{20}H_{12}(OH)_2} + 2FeCl_2 + HCl.$$

a-Dinaphthol forms silvery rhombic plates, which melt at 300° (572° F.); it gives a red colour with ferric chloride, and a violet precipitate with nitric acid. *β*-Dinaphthol crystallizes from alcohol in broad quadrangular prisms which melt at 218° (412°·4 F.); it gives a greenish colour with ferric chloride, and a dark green with nitric acid. Both these substances are insoluble in water, but easily soluble in alcohol or ether; they are dissolved by alkalies. It is said that they are reconverted into the corresponding naphthols when distilled. The dibenzoate of *a*-dinaphthol melts at 254° (489°·2 F.); that of the *β*-compound at 160° (320° F.) (Dianin, *Deut. chem. Ges. Ber.*, vi. 1252; vii. 125, 487).

§ IX. Trihydric Alcohols.—Alcohols of the $C_nH_{2n-1}(OH)_3$ Series.

Very few trihydric alcohols are at present known, this series including only two members, besides which we are acquainted with five trihydric alcohols derived from hydrocarbons of the benzene series, and a trioxynaphthalene.

(1530) GLYCERIN; *Glycerol:* $CH_2(OH).CH(OH).CH_2(OH)$.—This alcohol was discovered in 1779, by Scheele, when preparing lead plaster by saponifying lard with plumbic oxide. Most of the fixed oils and fats, from both animal and vegetable sources, are normal glyceric salts of acids of the acetic or oleic series, and yield glycerin when decomposed with alkalies or the more basic oxides. For example, it may be obtained from olive oil by heating the latter with rather more than half its weight of plumbic oxide and a little water until completely saponified, removing the insoluble plumbic oleate or lead plaster, precipitating the lead which remains in solution by sulphuretted hydrogen, and evaporating the aqueous solution:

$$\underset{\text{Olein or glyceric oleate.}}{2C_3H_5(C_{18}H_{33}O_2)_3} + 3PbO + 3OH_2 = \underset{\text{Glycerin.}}{2C_3H_5(OH)_3} + \underset{\text{Plumbic oleate.}}{3(C_{18}H_{33}O_2)_2Pb.}$$

Glycerin has been artificially prepared from *a*-trichloropropane, $CH_2Cl.CHCl.CH_2Cl$ (p. 159), by heating it with water to 170° (338° F.) (Friedel and Silva, *Compt. Rend.*, lxxiv. 805).

Pasteur has shown (*Ann. Chim. Phys.* [3], lviii. 355) that glycerin is always produced in the alcoholic fermentation of sugar, so that it occurs in all fermented liquors; according to his experiments, for every 100 parts of cane-sugar fermented, about 3·5 parts of glycerin are formed.

Preparation.—Glycerin is generally prepared from bye products of manufacturing operations, or is obtained as a subsidiary product in the preparation of solid fatty acids in the candle manufacture.

It may be obtained from spent soap lyes left after the soap has been salted out, or from the liquors separated from the insoluble mixture of lime soap and fatty acid formed in the first stage of the manufacture of stearin candles by saponifying tallow with milk of lime. In the former case the solution is first carefully neutralized with sulphuric acid; in the latter sulphuric acid is added, the solution boiled to expel volatile acids, and then carefully neutralized with lime: the dilute brown coloured solution of glycerin thus obtained is evaporated to the consistence of a syrup, and subsequently distilled in a current of superheated steam.

Mr. Tilghman found that when a mixture of fat and water was subjected for a short time to a temperature about that of melted lead, by forcing it through heated iron tubes, the former was decomposed, yielding a fatty acid, and an aqueous solution of glycerin which only required to be concentrated to be at once fit for use. A process somewhat similar to this in principle is now almost universally employed in this country, a patent having been taken out for that purpose by Messrs. Wilson and Payne, 24 July, 1854. The fat is charged into a still, which is gently heated externally, superheated steam being blown into the fat so as to maintain the temperature at about 288°—316° (550°—600° F.); by this means the fat is decomposed, and both the fatty acid and the glycerin distil over and condense in a pure state together with the aqueous vapour. By employing a series of condensors, the first of which are not cooled externally, the glycerin is obtained in a very concentrated state, the water condensing in the cooler part of the apparatus; or the aqueous solution of glycerin may be concentrated by evaporation.

Glycerin at the ordinary temperature is a syrupy, colourless liquid, inodorous, and of a sweet taste, readily absorbing moisture from the air. Exposed to a low temperature and continued vibration for some time, it solidifies to a crystalline mass, if pure and anhydrous. The crystals are rhombic prisms, and melt at 17° (Henninger, *Deut. chem. Ges. Ber.*, viii. 643); according to Roos (*Chem. Soc. Journ.*, 1876, i. 651), they melt at 15°·5 (60° F.), and the liquid glycerin at that temperature has a specific gravity of 1·261. Glycerin is miscible in all proportions with water, alcohol, or chloroform, but is insoluble in ether. It is slightly volatile at 100° (212° F.), but cannot be distilled under the ordinary atmospheric pressure as the greater portion undergoes decomposition with formation of acroleïn. It passes over readily, however, in a current of superheated steam at a temperature of 260°—315°·5 (500°—600° F.). It also distils without change under diminished pressure, boiling at 179°·5 (355° F.) under a pressure of 12·5 mm., and at 210° (410° F.) under a pressure of 50 mm. (Bolas); at 179° (354°·2 F.) under a pressure of 20 mm. (Henninger). Glycerin dissolves many substances which are but slightly soluble in water, taking up one-fifth of its weight of arsenious oxide, and dissolving iodine in large quantity.

Sodium has little or no action on glycerin in the cold, but on heating, hydrogen is rapidly evolved, the sodium becomes red-hot, and the glycerin is decomposed. A monosodium derivative of glycerin may be prepared, however, by dissolving sodium in alcohol and adding glycerin; after a time a crystalline deposit is formed of the composition $C_3H_7NaO_3,C_2H_6O$, which when heated to 100° (212° F.) in a current of hydrogen loses the alcohol of crystallization. Sodium glycerin is a white amorphous powder, which attracts moisture with the greatest avidity from the air; it is immediately decomposed by water (Letts, *Chem. Soc. Journ.*, xxv. 450). Calcic, strontic, and baric hydrates are freely soluble in glycerin, forming solutions which may be diluted with water, and in which carbonic anhydride produces no precipitate. Plumbic oxide is also dissolved by glycerin.

When glycerin is carefully added to the strongest nitric acid cooled by a mixture of ice and salt, and the solution is afterwards gradually mixed with concentrated sulphuric acid, glyceric trinitrate, $C_3H_5(NO_3)_3$, separates as a yellow oil, slightly soluble in water. This compound—the so-called nitroglycerin—is violently explosive, but requires the fulfilment of certain special conditions for the full development of its explosive force. Its explosion by the simple application of heat can only be accomplished if the source of heat be applied for a protracted period in such a way that chemical decomposition is established in some portion of the mass, and is favoured by the continued application of heat to that part. Under these circumstances the change proceeds with very rapidly accelerating violence, and the sudden transformation into gaseous products of the heated mass ultimately takes place—a transformation which is instantly communicated throughout the mass, so that the confinement of the substance is not necessary to develop its full explosive force. This result can be obtained more expeditiously and with greater certainty by exposing the substance to the concussive action of a detonation produced by the ignition of a small quantity of fulminating powder, closely confined and placed either in contact with, or in proximity to the nitrate (Abel, *Phil. Trans.*, 1869; *Chem. Soc. Journ.*, xxiii. 41). It also detonates when struck. By the action of alkalies, or reducing agents, glyceric trinitrate is reconverted into glycerin; thus, when it is heated with an aqueous solution of potassic hydrate, glycerin and potassic nitrate are obtained, and on mixing it with a concentrated solution of hydriodic acid, glycerin is produced with evolution of pure nitric oxide (Mills). The lower nitrates, $C_3H_5(OH)(NO_3)_2$ and $C_3H_5(OH)_2(NO_3)$, are probably formed by the moderated action of nitric acid on glycerin, but they are not known in the pure state.

On mixing glycerin with concentrated sulphuric acid, hydric glyceric sulphate, $SO_2(OH).O.C_3H_5(OH)_2$, is produced; and by the action of phosphoric acid or anhydride, glycerin is converted into the acid phosphate, $PO(OH)_2.O.C_3H_5(OH)_2$. The latter compound is of especial importance, as it forms, so to speak, the framework upon which all the highly complex phosphorized constituents of the brain, &c., are constructed.

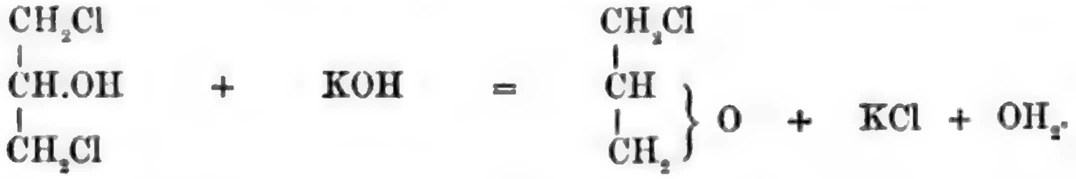
By heating glycerin with organic acids, ethereal salts are produced which vary in composition according to the proportions in which the substances are employed, the temperature and pressure to which the mixture is subjected, and the time for which the heating is continued. These salts are usually designated by names formed from those of the acids by changing the termination *ic* into *in*; thus acetic acid forms acetins, stearic acid forms stearins, and oleic acid forms oleins. The normal salts, or salts formed from glycerin by displacing the three atoms of hydrogen of the three hydroxyl groups by acid radicles, produced by heating glycerin with acids such as oleic and stearic acid, are identical with the stearin and olein of natural fats and fixed oils.

By the action of hydrochloric or hydrobromic acid on glycerin either one or two of the three hydroxyl groups may be displaced by chlorine or bromine; the third may be displaced by the action of pentachloride or pentabromide of phosphorus (p. 159).

To prepare the monochlorhydrin, $C_3H_5Cl(OH)_2$, glycerin is saturated with hydrochloric acid gas, and the solution maintained for some time at 100° (212° F.); it is then submitted to fractional distillation, the portion which boils at about 225°—230° (437°—446° F.) being collected apart. It is not known whether the product obtained in this way, which is a viscid liquid soluble in water, contains both the possible monochlorhydrins of glycerin, but it certainly consists chiefly of *chloromethylglycol*, $CH_2Cl.CH(OH).CH_2(OH)$, as on treating its aqueous solution with sodium amalgam methylglycol, $CH_3.CH(OH).CH_2(OH)$, is obtained (Buff, *Ann. Chem. Pharm. Supp.*, v. 247). The isomeric compound, *chloro-a-propylenic glycol*, $CH_2(OH).CHCl.CH_2(OH)$, is formed on mixing allylic alcohol with a dilute aqueous solution of hypochlorous acid, but the yield is very small, as much of the alcohol is oxidized; it boils at about 220° (428 F.) (Henry, *Deut. chem. Ges. Ber.*, v. 449).

The dichlorhydrins of glycerin are formed on heating a mixture of 1 volume of glycerin and 12 volumes of hydrochloric acid for some time to 100° (212° F.), and then distilling the mixture; a better method of preparation is to saturate a mixture of equal volumes of glycerin and glacial acetic acid with hydrochloric acid, finally at 100° (212° F.), and to isolate the product by fractional distillation. In this way a mixture of the two compounds, $CH_2Cl.CHCl.CH_2(OH)$ or dichloropropylic alcohol, and $CH_2Cl.CH(OH).CH_2Cl$, or dichlorisopropylic alcohol, is obtained, the latter being the chief product, however (Hübner and Müller, *Ann. Chem. Pharm.*, clix. 170); apparently the tendency for the former to be produced is less the higher the temperature at which the action takes place, so that if the mixture be heated to about 120° (248° F.), and saturated with hydrochloric acid, almost pure dichlorisopropylic alcohol is formed. An extremely good method for preparing the latter is to add the chloride of sulphur S_2Cl_2 to anhydrous glycerin, which is heated in a salt-bath, until no further action takes place; the liquid product is poured off from the cake of sulphur, washed with water and a small quantity of sodic carbonate, dried, and purified by distillation (Carius). According to Claus (*ibid.*, clxviii. 42), the action which takes place is expressed by the equation: $C_3H_5(OH)_3 + 2S_2Cl_2 = C_3H_5Cl_2(OH) + SO_2 + 2HCl + 3S$; he recommends the addition of 2000 grams of the chloride to 800 grams of glycerin which has been rendered anhydrous by heating to 195° (383° F.) in an open dish. The product is separated from the sulphur by ether, and the residue left on distilling off the ether is submitted to fractional distillation. *Dichloropropylic alcohol* is best prepared by passing chlorine into well cooled anhydrous allylic alcohol; it is a somewhat mobile liquid, of the specific gravity 1·389 at 0° (32° F.), soluble in a large quantity of water; it boils at about 182° (359°·6 F.) (Tollens, *ibid.*, clvi. 165; p. 466). *Dichlorisopropylic alcohol*, like its isomeride, is a colourless liquid of agreeable odour, soluble in about nine times its volume of water; it boils at 176° (348°·8 F.), and at 17°·5 (63°·5 F.) has the specific gravity 1·366. On treating its aqueous solution with sodium amalgam, isopropylic alcohol is obtained (Buff), but by the action of sodium on its ethereal solution, allylic alcohol is produced (Hübner and Müller); allylic alcohol is obtained from the isomeric dichlorhydrin on treating the aqueous solution with sodium amalgam (Tollens). The compound $CH_2Cl.CH(OH).CH_2Cl$ is usually termed simply dichlorhydrin.

Both the dichlorhydrins of glycerin are converted into the same compound—the so-called epichlorhydrin or chloropropylenic oxide—by the action of alkalies:



$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH \\ | \\ CH_2Cl \end{array} \quad + \quad KOH \quad = \quad \left.\begin{array}{l} CH_2Cl \\ | \\ CH \\ | \\ CH_2 \end{array}\right\} O \quad + \quad KCl \; + \; OH_2.$$

Dichlorisopropylic alcohol. Chloropropylenic oxide.

The best method of preparing epichlorhydrin appears to consist in adding gradually a nearly saturated aqueous solution of 300 grams of sodic hydrate to 500 grams of the crude mixture of the two dichlorhydrins and of chloracetins boiling at 140°—220° (284°—428° F.), obtained by saturating a mixture of glycerin and acetic acid with hydrochloric acid, and then distilling; the action, which is at first extremely violent, is completed by well agitating the mixture and warming on the water bath (Patzschke, *Journ. pr. Chem.* [2], i. 82; Hübner and Müller, *loc. cit.*). The product is separated, washed with small quantities of water, dried over anhydrous cupric sulphate, and purified by fractional distillation. It is a colourless, mobile liquid, insoluble in water, possessing an agreeable odour like that of chloroform; it boils at 118°—119° (244°·4—246°·2 F), and at 11° (51°·8 F.) has the specific gravity 1·194. On heating it with water under pressure, it is converted into the monochlorhydrin of glycerin, $CH_2(OH).CH(OH).CH_2Cl$. It readily combines with hydrochloric acid forming the dichlorhydrin $CH_2Cl.CH(OH).CH_2Cl$, much heat being developed on adding a concentrated solution of the acid; the conversion is completed by passing hydrochloric acid gas into the mixture, and then warming gently for some time. In this manner the pure dichlorhydrin may readily be prepared from glycerin, by first preparing the mixture of dichlorhydrins and converting the latter into epichlorhydrin. By acting on an ethereal solution of epichlorhydrin with sodium and treating the product with water, Hübner and Müller (*loc. cit.*, p. 184) have obtained a compound which they regard as a dihydric alcohol of the composition $C_6H_{10}(OH)_2$; but its properties have not yet been investigated.

On heating dichlorhydrin with a one per cent. alcoholic solution of ammonia in closed vessels at about 105° (221° F.) the hydrochlorides of two bases—*diamidohydrin* and *glycidamine*—are produced, one of which may be regarded as formed from dichlorhydrin by the displacement of the two atoms of chlorine by twice the group NH_2, and the other as bearing a similar relation to epichlorhydrin. By the action of a 4 per cent. solution, however, a far more complex substance, *chlorhydrinimide*, $C_{12}H_{27}N_3Cl_2O_4$, is formed; this body is remarkable on account of its extreme stability, being unaffected when boiled with concentrated hydrochloric, nitric, or sulphuric acid, or a concentrated solution of potassic hydrate (Claus, *Ann. Chem. Pharm*, clxviii. 29).

Dichlorhydrin is readily acted on by bromine when heated with it to about 100° (212° F.); there has been much discussion as to the nature of the product, but from the latest experiments of Carius it appears that it chiefly consists of a dibromodichloracetone, (?) $CH_2Cl.CO.CBr_2Cl$, which is capable of combining with water to form a crystalline hydrate $C_3H_2Br_2Cl_2 + 4H_2O$ (*Ann. Chem. Pharm.*, clv. 35). By reducing this hydrate with zinc and sulphuric acid, Lange has obtained acetone (*Deut. chem. Ges. Ber.*, vi. 98).

Little is known of the bromhydrins produced by the action of hydrobromic acid on glycerin. The dibromhydrin $CH_2Br.CHBr.CH_2(OH)$ is obtained by the direct combination of bromine with allylic alcohol (p. 466), by adding bromine to a mixture of the alcohol and water, or by placing a dish containing the necessary amount of bromine in a bell jar containing the alcohol and immersed mouth upwards in a pail of water, the mouth of the jar being covered with a glass plate; the combination then gradually takes place. The product must be distilled in a current of steam before it is distilled alone (Münder and Tollens, *Ann. Chem. Pharm.*, clxvii. 224). It is a heavy oily liquid, boiling at about 212°—214° (413°·6—417°·2 F.); according to Linnemann (*Deut. chem. Ges. Ber.*, vii. 858), the product of the action of bromine on allylic alcohol in presence of water may be separated, by washing with successive small quantities of water, into an easily soluble and a difficultly soluble portion: the former requiring three to four times, and the latter about 34 times its volume of water for complete solution; the nature of the two substances has not yet been ascertained.

Epibromhydrin, C_3H_5BrO, is obtained by the action of alkalies on the dibromhydrins of glycerin; it boils at 138°—140° (280°·4—284° F.). Epichlorhydrin combines with hydrobromic acid with great readiness; the product, $CH_2Cl.CH(OH).CH_2Br$, which resembles the dichlorhydrins, boils at 197° (386°·6 F.), and at 12° (53°·6 F.) has the specific gravity 1·740. The same substance is obtained by combining epibromhydrin with hydrochloric acid. Epichlor- and epibromhydrin also combine with hydriodic acid, much heat being developed on mixing them with a concentrated solution of the acid; the chloriodhydrin boils at about 226° (438°·8); the bromiodhydrin cannot be distilled (Reboul, *Ann. Chem. Pharm. Supp.*, i. 224; Henry, *Deut. chem. Ges. Ber.*, iii. 351, 600).

By the action of a mixture of concentrated nitric and sulphuric acids on the mono- and dichlorhydrin of glycerin, the nitrates $C_3H_5Cl(NO_3)_2$ and $C_3H_5Cl_2(NO_3)$ are produced; the former is an oily liquid, and boils at 180°—190° (356°—374° F.), but with partial decomposition; the latter, which is also obtained by the action of nitric acid on epichlorhydrin, is not volatile (Henry, *ibid.*, p. 347).

By heating a saturated solution of hydriodic acid gas in glycerin for 40 hours to 100° (212° F.), and, after removing the excess of acid with an alkali, extracting the product with ether, Berthelot and Lucca obtained a syrupy substance to which they attribute the formula $C_6H_{11}IO_6$; this may perhaps have been the impure moniodhydrin $C_3H_5I(OH)_2$. By heating the dichlorhydrin $CH_2Cl.CH(OH)\,CH_2Cl$ with an aqueous solution of potassic iodide to 105°—110° (221°—230° F.) it is converted into the corresponding diiodhydrin; this compound is a viscid liquid of the specific gravity 2·4 at 15° (59° F.), almost insoluble in water, and decomposes on distillation. It solidifies when cooled to about − 20° (− 4° F.) (Claus, *Ann. Chem. Pharm.*, clxviii. 21). Epichlorhydrin may in a similar manner be converted into epiiodhydrin by heating it with dry potassic iodide to 100° (212° F.); epiiodhydrin is a colourless mobile liquid of the specific gravity 2·03 at 15° (55°·4 F.), and boils at about 160° (320° F.) (Reboul, *loc. cit.*).

When submitted to the action of iodide of phosphorus, or of a concentrated solution of hydriodic acid, glycerin yields a mixture of allylic and isopropylic iodides with propylene, the proportions in which these substances are formed being dependent upon the proportions in which the materials are employed: allylic iodide being chiefly produced if the glycerin be in excess, but isopropylic iodide if the acid or iodide of phorphorus be in excess* (Erlenmeyer, *Ann. Chem. Pharm.*, cxxxix. 211). The precise manner in which the allylic iodide is formed has yet to be ascertained; probably, triiodopropane is first produced, but immediately decomposes into allylic iodide and iodine, thus:

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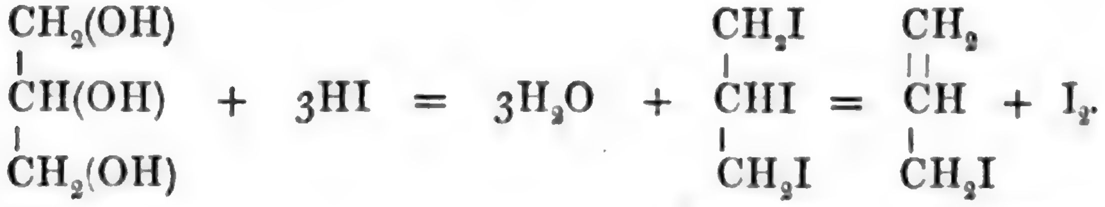
* According to Oppenheim 1500 grams of glycerin, 1000 grams of iodine, and 600 of phosphorus furnish on an average 750 grams of allylic iodide boiling



$$\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array} + 3HI = 3H_2O + \begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array} + I_2.$$

Glycerin. Triiodopropane. Allylic iodide.

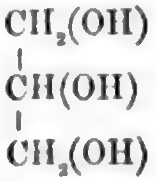
This reaction is obviously comparable with that which occurs on adding potassic iodide to a solution of cupric sulphate, cuprous and not cupric iodide being obtained in consequence of the decomposition of the latter immediately on formation:

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

The isopropylic iodide and propylene are doubtless both products of secondary action, and in all probability are formed from the allylic iodide (pp. 161, 207).

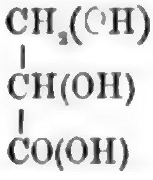
Glycerin is very readily oxidized to carbonic acid and water, but when carefully oxidized by nitric acid it yields glyceric acid (Debus) and apparently, under certain conditions, tartronic acid (Sadtler, *Deut. chem. Ges. Ber.*, viii. 1456), together with racemic, glycolic, glyoxylic, oxalic, and formic acids (Heintz, *Ann. Chem. Pharm.*, clii. 325).

The relation of the two first-mentioned acids to glycerin is indicated by the following formulæ:



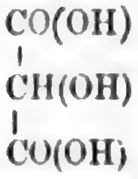
$$\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array}$$

Glycerin.



$$\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CO(OH) \end{array}$$

Glyceric acid.



$$\begin{array}{l} CO(OH) \\ | \\ CH(OH) \\ | \\ CO(OH) \end{array}$$

Tartronic acid.

The formation of racemic acid is not yet satisfactorily explained. It might be supposed that it is formed either by the simultaneous oxidation of glyceric and formic acids in the same way that benzoic acid is produced by oxidizing a mixture of benzene and formic acids (p. 260), thus:

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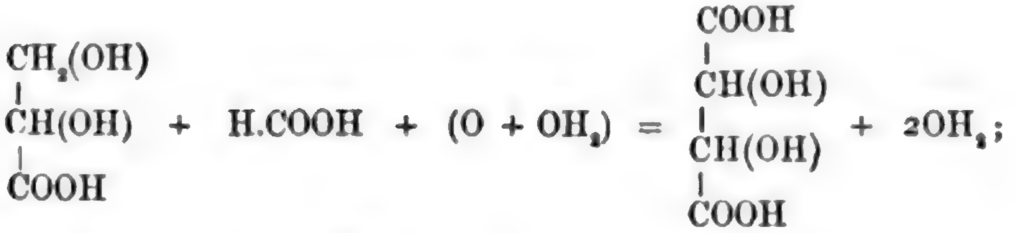
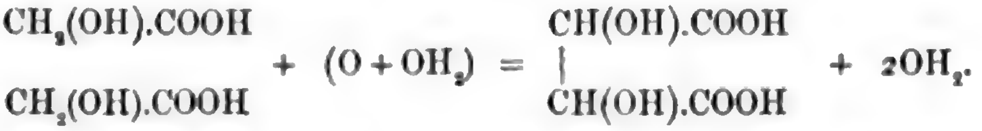
at 98°—103° C., 200 grams of a mixture of isopropylic and allylic iodides boiling at 90°—98° C., and sufficient propylene to combine with about 100 grams of bromine. For a description of the method of preparing allylic iodide from glycerin see Claus, *Ann. Chem. Pharm.*, cxxxi. 58, and Oppenheim, *ibid. Supp.*, vi. 354; the best method, however, of obtaining it, is from allylic alcohol (p. 207), as it is impossible entirely to separate the two iodides by fractional distillation. The preparation of isopropylic iodide is described in Watts' Dictionary, v. 890.



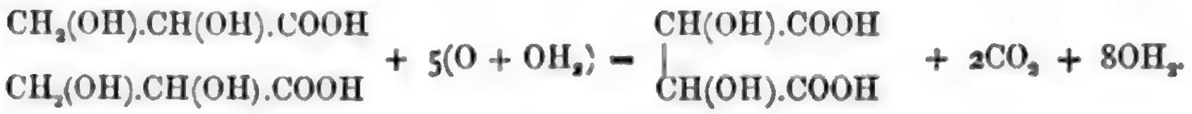
$$\begin{array}{l}\mathrm{CH_2(OH)}\\ | \\ \mathrm{CH(OH)}\\ | \\ \mathrm{COOH}\end{array} + \mathrm{H.COOH} + (\mathrm{O} + \mathrm{OH_2}) = \begin{array}{l}\mathrm{COOH}\\ | \\ \mathrm{CH(OH)}\\ | \\ \mathrm{CH(OH)}\\ | \\ \mathrm{COOH}\end{array} + 2\mathrm{OH_2};$$

or from two molecules of glycolic acid:



$$\begin{array}{l}\mathrm{CH_2(OH).COOH}\\ \\ \mathrm{CH_2(OH).COOH}\end{array} + (\mathrm{O}+\mathrm{OH_2}) = \begin{array}{l}\mathrm{CH(OH).COOH}\\ | \\ \mathrm{CH(OH).COOH}\end{array} + 2\mathrm{OH_2}.$$

Heintz, however, failed to obtain the acid in this manner; but as only a single experiment to test each of these explanations was made, his want of success can scarcely be regarded as a proof that racemic acid cannot be produced in accordance with either of the reactions expressed by these equations, as doubtless special conditions are requisite for its formation which may not have been secured. It is possible also that racemic acid is a direct oxidation product of glyceric acid itself:



$$\begin{array}{l}\mathrm{CH_2(OH).CH(OH).COOH}\\ \\ \mathrm{CH_2(OH).CH(OH).COOH}\end{array} + 5(\mathrm{O} + \mathrm{OH_2}) = \begin{array}{l}\mathrm{CH(OH).COOH}\\ | \\ \mathrm{CH(OH).COOH}\end{array} + 2\mathrm{CO_2} + 8\mathrm{OH_2}.$$

A possible, although perhaps not very probable, explanation is that it is derived from a foreign substance present in the glycerin.

When glycerin is gently heated with potassic hydrate, it is converted into potassic acetate and formate, with evolution of hydrogen.

On distillation with phosphoric anhydride, or hydric potassic sulphate, it yields acrylic aldehyde or acroleïn, C_3H_4O.

According to Claus (*Deut. chem. Ges. Ber.*, ix. 695), when a pasty mixture of glycerin and zinc dust is submitted to distillation, a mixture of propylene and hydrogen gas is evolved, from 30 to 45 litres of gas, about half consisting of propylene, being obtained from 100 grams of glycerin.

A number of experiments have been made as to the power of glycerin to undergo fermentation.

It was first noticed by Redtenbacher in 1846 that, when a dilute aqueous solution of glycerin, mixed with washed beer yeast, was exposed to the air at a temperature of 20°—30° (68°—86° F.), the liquid after a time became acid and gas was slowly evolved, the yeast partly rising to the surface and growing mouldy. The acid was neutralized from time to time by sodic carbonate, the yeast distributed through the liquid by stirring, and fresh water added to replace that lost by evaporation; when the solution no longer became acid on standing, it was acidified with sulphuric acid and distilled. From the acid distillate a silver salt was prepared having all the properties and the composition of that of propionic acid, $C_3H_6O_2$, and the mother liquor from this salt deposited crystals which Redtenbacher regarded as a double salt of argentic acetate and propionate (*Ann. Chem. Pharm.*, lvii. 174).

Berthelot, in 1856, stated that a solution of glycerin undergoes fermentation in presence of chalk and casein, or other animal substances, at a temperature of about 40° (104° F.), a small quantity of alcohol being produced. According to Béchamp (*Compt. Rend.*, lxix. 669) however, the product is more complex: for on exposing mixtures of 250 grams glycerin dissolved in 3000 grams of water, 125 grams of chalk, and 30 grams of chopped mutton, to a temperature of 35°—40° (95°—104° F.) for eight months, he obtained as the fermentation product of about 450 grams of glycerin no less than 148 grams of anhydrous alcohol mixed with higher homologues, and 132 grams of a mixture of acids; the acids were not specially identified, but from the boiling points observed on distilling the mixture, Béchamp considered that acetic, propionic, butyric, valeric, and capronic acids are formed.

Horace Brown (*private communication*) finds that although fermentation takes place when a solution of commercial glycerin is mixed with beer yeast and chalk, it very soon ceases, and cannot again be excited by the addition of more yeast. From this observation, it appears not improbable that ordinary glycerin contains a small quantity of a fermentable substance—a supposition which derives support from the fact that, according to Roos (*Journ. Chem. Soc.*, 1876, i. 651), *pure* glycerin in contact with washed German yeast undergoes no change. Fitz also states that glycerin does not undergo change in contact with ferments which excite alcoholic fermentation (*Deut. chem. Ges. Ber.*, ix. 1348), but he has found that it rapidly ferments in contact with a species of *bacterium*, which he has not yet described. Fitz employs a mixture of 2000 pts. water, 100 pts. glycerin, 1 pt. potassic phosphate, ·5 pt. magnesic sulphate, 20·0 pts. calcic carbonate, and 2·0 pts. pepsin, to which a trace of the ferment is added, exposing it to a temperature of about 40° (104° F.). Vigorous fermentation sets in within two days at latest, and is complete in ten days, carbonic anhydride and hydrogen gases being evolved; on distilling the liquid, &c., a product is obtained consisting of ethylic and *normal* primary butylic alcohol in the proportion of about 1 : 5, and from the residue in the retort, normal butyric acid containing a small quantity of caproic acid is liberated on distillation with hydrochloric acid. In this manner 7·7 grams of butylic alcohol and 12·3 grams of anhydrous calcic butyrate were obtained from 100 grams of glycerin, so that the fermentation of glycerin affords a ready means of preparing normal butylic alcohol.

(1531) *Polyglyceric Alcohols.*—These compounds are related to glycerin in the same way that the polyethylenic alcohols (p. 512) are related to glycol. They are obtained by heating glycerin with its monochlorhydrin, and apparently are products of the decomposition of glycerin by heat. To prepare them, glycerin diluted with one-third its bulk of water is saturated at 100° (212° F.) with hydrochloric acid gas, a quantity of glycerin equal to that at first taken is added, and the mixture heated to 130° (266° F.) in a flask attached to a reversed condenser for 12 to 15 hours; on distilling, water and hydrochloric acid pass over until the temperature rises to 150° (302° F.), then between 150° and 275° (302° and 527° F.), a mixture of dichlorhydrin and of the mono- and dichlorhydrins of diglyceric alcohol. By distilling the residue under a pressure of 10 mm. of mercury, it is separated into a portion boiling at 220°—230° (428°—446° F.), and another boiling at 275°—285° (527°—545° F.),—which constitute respectively *diglyceric* and *triglyceric* alcohol, $C_6H_{14}O_5$ and $C_9H_{20}O_7$—leaving a residue consisting of still more complex substances. Diglyceric alcohol is very viscid, insoluble in ether, soluble in hot but sparingly soluble in cold water, and is dissolved by alcohol in all proportions; triglyceric alcohol is a similar but still more viscid body (Lourenço, *Compt. Rend.*, lii. 359).

(1532) *Amylic glycerol:** $C_5H_9(OH)_3$.—This compound was prepared by Bauer by the following series of reactions (*Jahresb.*, 1861, p. 664). Amylenic bromide, $C_5H_{10}Br_2$ (prepared doubtless from the crude amylene from fermentation amylic alcohol and zinc chloride), was converted into bromamylene, C_5H_9Br, by the action of an alcoholic solution of potassic hydrate, and the latter compound converted into the tribromide $C_5H_9Br_3$ by treatment with bromine; by heating the tribromide with an alcoholic solution of argentic acetate, the diacetate $C_5H_9Br(C_2H_3O_2)_2$ was obtained, which was then converted by saponification into the bromoglycol $C_5H_9Br(OH)_2$; finally, an ethereal solution of this compound was heated with potassic hydrate in closed tubes on the water bath. Amylglycerol is stated to be a viscid substance, soluble in water, and having a sweet aromatic taste.

§ X. TRIHYDRIC ALCOHOLS OF THE $C_nH_{2n-9}(OH)_3$ SERIES.

(1533) This series includes the following alcohols:

Pyrogallol or (?) metatrioxybenzene . . .	$C_6H_3(OH)_3$
Phloroglucol or (?) paratrioxybenzene . . .	
Dimethylmetatrioxybenzene	$C_6H(CH_3)_2(OH)_3$
Phenylglycerol	$C_6H_5.C_3H_4(OH)_3$
Propylmethylmetatrioxybenzene	$C_3H_7.C_6H(CH_3)(OH)_3$.

(1534) **PYROGALLOL**; *Pyrogallic Acid*: $C_6H_3(OH)_3$. (?) *Metatrioxybenzene* (OH : OH : OH = 1 : 2 : 4).—This compound is the product of the decomposition of gallic acid by heat: $C_6H_2(OH)_3.COOH = C_6H_3(OH)_3 + CO_2$.

It may be obtained by heating a dried aqueous extract of galls in a shallow pan covered with a sheet of filtering paper, over which a cone of ordinary paper is pasted, the temperature being maintained as nearly as possible at about 180° (356° F.) for several hours; a yield of about 5 per cent. is thus obtained. According to Liebig (*Ann. Chem. Pharm*, ci. 47), the best method of preparing it is to heat gallic acid mixed with twice its weight of coarsely powdered pumice in a retort through which a current of dry carbonic anhydride is passed: 30 to 32 parts of pyrogallol are in this way obtained for every 100 parts of gallic acid employed. De Luynes and Esperandieu, however, state that the theoretical amount of pyrogallol may be obtained from gallic acid by heating it with twice or thrice its weight of water to 200°—210° (392°—410° F.) in a bronze Papin's digestor for about half an hour; the solution from the digestor is boiled with a little animal charcoal, evaporated to dryness, and the residue distilled under a pressure of 20—30 mm. of mercury (*ibid*, cxxxviii. 60).

By heating diiodosalicylic acid, $C_6H_2I_2(OH).COOH$, with a very concentrated aqueous solution of potassic hydrate, Lautemann (*ibid.*, cxx. 299) obtained a product which he regarded as a mixture of gallic acid and pyrogallol, and by subliming this he obtained a substance exhibiting all the properties of pyrogallol, but the quantity was too small for analysis. From Demole's experiments (*Deut. chem. Ges. Ber.*, vii. 1439), it appears that Lautemann's diiodo-acid (M.P.

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* The termination *ol* may conveniently be employed for alcohols generally, and its use restricted to alcohols. Further, just as the homologues of methylic alcohol and monohydric alcohols having similar properties are termed *carbinols*, and dihydric alcohols allied to glycol are termed *glycols*, so we may term trihydric alcohols related to glycerol (glycerin) *glycerols*, tetrahydric alcohols resembling erythrol (erythrite) in their properties *erythrols*, &c. &c.—[EDS.]

212° C.) was impure, and according to this chemist the purified acid melting at 220°—230° (428°—446° F.) does not yield gallic acid or pyrogallol on treatment with potassic hydrate, but a mixture of the two dioxybenzoic acids—oxysalicylic acid and protocatechuic acid.

According to Petersen and Baehr-Predari (*Ann. Chem. Pharm.*, clvii. 136), pyrogallol is formed on heating the potassium salt of parachlorophenolorthosulphonic acid, $C_6H_3Cl(OH).SO_3H$, with potassic hydrate at about 160° (320° F.) &c.

Pyrogallol crystallizes in long, colourless, flattened prisms, bitter to the taste, soluble in 2½ pts. of water at 12° (53°·6 F.); it melts at 115° (239° F.), and may readily be distilled under reduced pressure. On heating to about 250° (482° F.) it loses the elements of water and is converted into the so-called metagallic acid, a black amorphous substance, insoluble in water but soluble in alkalies.

When passed over heated zinc dust, pyrogallol is reduced to benzene (Baeyer). Pyrogallol has very feeble acid properties, its solution being rendered alkaline by the addition of the smallest quantity of an alkali. On passing ammonia into an ethereal solution of pyrogallol, a white crystalline precipitate of the ammonium derivative $C_6H_3(OH)_2(ONH_4)$ is produced (De Luynes and Esperandieu); an aqueous solution acidulated with acetic acid yields a precipitate on the addition of plumbic acetate which, after drying first over sulphuric acid, and then at 120° (248° F.) in a current of dry hydrogen, has the composition $C_{12}H_{20}PbO_6$, $(C_2H_3O_2)_2Pb$ (Deering, *Chem. Soc. Journ.*, xxvi. 702); the antimony derivative $C_6H_3(OH)_2(O.SbO)$ separates in glistening plates on adding a moderately concentrated solution of pyrogallol to a boiling solution of tartar emetic. Pyrogallol dissolves in acetic chloride, being converted into the triacetate $C_6H_3(C_2H_3O_2)_3$; this compound forms small white crystals almost insoluble in cold water, but soluble in alcohol.

When bromine is added to an aqueous solution of pyrogallol, it is oxidized, but the nature of the reaction has not yet been investigated. On adding dry bromine to dry pyrogallol, or to its solution in glacial acetic acid, however, it is converted into *tribromopyrogallol*, $C_6Br_3(OH)_3$. This compound is very sparingly soluble in cold water, more soluble in hot water, but is decomposed by long boiling; it crystallizes from alcohol in large prisms containing a molecule of water. On treatment with bromine in presence of water it is converted into a yellow crystalline substance, *xanthogallol*, $C_{18}H_4Br_{14}O_6$, of unknown constitution (Stenhouse, *Chem. Soc. Journ.*, xxviii. 1). Neither nitro- nor chloro-derivatives of pyrogallol are known, but by the action of chlorine on a solution of pyrogallol in glacial acetic acid, two complex chlorinated compounds, *mairogallol*, $C_{18}H_7Cl_{11}O_{10}$, and *leucogallol*, $C_{18}H_{10}Cl_{12}O_{14}$, are obtained (Stenhouse and Groves, *ibid.*, xxviii. 704). By warming pyrogallol with anhydrosulphuric acid it is converted into the monosulphonic acid $C_6H_2(OH)_3.SO_3H$ (Schiff, *Deut. chem. Ges. Ber.*, v. 663—1055); according to Personne (*ibid.*, vi. 1419), pyrogallol furnishes a disulphonic acid on treatment with concentrated sulphuric acid.

Pyrogallol is very readily oxidized, and although the dry substance does not change when exposed to the air, its solution absorbs oxygen, turning brown; an aqueous solution of potassic hydrate and pyrogallol absorbs oxygen with such avidity that it is often employed for removing that element from gaseous mixtures. Calvert, Cloez, and Boussingault (*Ann. Chem. Pharm.*, cxxx. 248) have shown that in the oxidation of an alkaline solution of pyrogallol a small quantity (from 1 to nearly 4 per cent. of the oxygen absorbed) of carbonic oxide gas is produced, the amount depending upon the concentration and the intensity of the action: more being formed when pure oxygen is employed than when it is mixed with an indifferent gas. By the continued action of oxygen or ozone on the alkaline liquid, the dark colour after a time becomes reddish-yellow and then yellow; Boeke (*Deut. chem. Ges. Ber.*, vi. 486) has found that if a solution of 10 grams of pyrogallol and 13·33 grams of potassic hydrate be submitted in small portions to the action of a stream of ozonized oxygen until it becomes reddish-yellow—an operation which requires several weeks—a strongly alkaline liquid is obtained, which evolves carbonic anhydride on the addition of acetic acid, the amount of acetic acid required to neutralize it indicating that the acid formed is sufficient to neutralize two-thirds of the potassic hydrate employed. On the addition of plumbic acetate to the slightly acid solution a precipitate was produced from which he obtained a crystalline acid of the composition $C_6H_6O_7$. When a solution of pyrogallol is cautiously treated with argentic nitrate, potassic permanganate, or chromic acid, orange-red flocks are obtained, which on crystallization from alcohol, or sublimation, yield deep red needles of purpurogallin or oxypyrogalloquinone (Girard, *Compt. Rend.*, lxix. 865; Wichelhaus, *Deut. chem. Ges. Ber.*, v. 846; Struve, *Ann. Chem. Pharm.*, clxiii. 160). This substance dyes mordanted fabrics somewhat like alizarin, but the colours are dull; its relation to quinone and to pyrogallol is indicated by the formula $C_6H_3(OH)\left\{\begin{matrix}O.O.C_6H_3(OH)_2\\O.O.C_6H_3(OH)_2\end{matrix}\right.$. Nitric acid converts pyrogallol into oxalic acid.

Pyrogallol reduces the salts of gold and silver, and on this account is extensively employed in photographic operations for the purpose of developing the latent image on the argentiferous collodion film after it has been exposed to the action of light. With a solution of ferrous containing traces of ferric sulphate, it gives a characteristic indigo blue colour, which rapidly becomes green and then red. When a solution of pyrogallol is added to milk of lime, a beautiful purple colour is produced, which soon becomes of a dirty brown, forming a delicate and characteristic test for the presence of pyrogallol.

(1535) PHLOROGLUCOL; *Phloroglucin*: $C_6H_3(OH)_3$. (?) *Paratrioxybenzene* (OH : OH : OH = 1 : 3 : 5).—This isomeride of pyrogallol is formed by the action of fused potassic hydrate on a great variety of substances, amongst which may be mentioned phloretin, quercetin, moritannic acid, horse chestnut tannin, catechin, scoparin, luteolin, dragon's blood and gamboge. It was first obtained by Hlasiwetz in 1855 from phloretin; according to Schiff (*Ann. Chem. Pharm.*, clxxii. 356), it is best prepared from this compound in the following manner:

Twenty grams of phloretin and 150 cc. of a solution of potassic hydrate of the specific gravity 1·20 are heated in a flask attached to a reversed condenser for about three hours; the cooled liquid is then poured into a litre cylinder in which all the remaining operations are effected. It is exactly neutralized with sulphuric acid, a very slight excess of sodic bicarbonate is added, and the phloroglucol extracted by agitating the solution with an equal volume of ether, the extraction with ether being repeated four times. If an excess of sulphuric acid be then added, the phloretic acid, which is the complementary product of the action of the alkali on phloretin, may be extracted in a similar manner.

On distilling off the ether, nearly colourless phloroglucin remains; it may be decolorized and purified by dissolving in water, and adding a small quantity of plumbic acetate, and passing sulphuretted hydrogen through the solution; it is then extracted by ether, and recrystallized from ether or water.

The best material for the preparation of phloroglucol, according to Hlasiwetz (*ibid.*, cxxxiv. 122), is kino, 100 grams (? 1000 grams) of which gave 92 grams of phloroglucin.

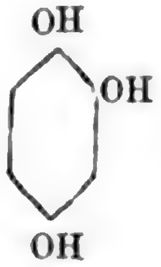
It separates from its aqueous solution in large trimetric prisms of the composition $C_6H_6O_3, 2OH_2$, which effloresce in dry air and are rendered anhydrous by heating to 90° (194° F.); the anhydrous substance melts at about 220° (428° F.), and may be sublimed at a higher temperature without decomposition. It has a sweeter taste than cane sugar, and is readily soluble in ether, less so in water or alcohol. On mixing an alcoholic solution of potassic hydrate with a concentrated alcoholic solution of phloroglucol, a potassium derivative separates as an oily mass, which becomes crystalline after a time; its composition has not yet been ascertained. Basic plumbic acetate produces a white precipitate of the composition $C_6H_3(OH)(O.PbOH)_2$ in solutions of phloroglucol. Acetic and benzoic chlorides readily act on it, forming the compounds $C_6H_3(C_2H_3O_2)_3$, and $C_6H_3(C_7H_5O_2)_3$. It dissolves in ammonia solution, and if the liquid be allowed to evaporate spontaneously, glistening crystals of *phloramine*, $C_6H_3(OH)_2(NH_2)$, are obtained; the same compound is formed by the action of gaseous ammonia. On adding bromine to a concentrated aqueous solution of phloroglucol, the *tribromo*-derivative $C_6Br_3(OH)_3$ separates as a crystalline pulp; it is very slightly soluble in cold water, easily in alcohol, crystallizing from the latter in long prisms of the compositions $C_6H_3Br_3O_3,3OH_2$, which lose their water of crystallization at 100° (212° F.). On passing chlorine into a cold aqueous solution of phloroglucol, *dichloracetic acid* is obtained (Hlasiwetz and Habermann, *ibid.*, clv. 132):

$$C_6H_3(OH)_3 + 6Cl_2 + 3OH_2 = 3CHCl_2.COOH + 6HCl.$$

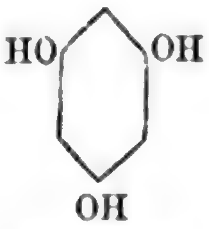
Nitric acid acts violently on phloroglucol and readily converts it into oxalic acid, but by gradually adding it to the somewhat dilute slightly warmed acid, it is converted into *trinitrophloroglucol*, $C_6(NO_2)_3(OH)_3$; it crystallizes from water, in which it is only slightly soluble when cold, in reddish-yellow glistening scales and plates (Hlasiwetz, *ibid.*, cxix. 199). Phloroglucol is readily converted by warming with phosphoric oxychloride into phloroglucid $C_{12}H_{10}O_5$ (Schiff, *ibid.*, clxxii. 358); this compound crystallizes with two molecules of water in colourless scales, slightly soluble in warm water and in alcohol, insoluble in ether (Hlasiwetz). Phloroglucol is converted into a crystalline monosulphonic acid by the action of the theoretical amount of anhydrosulphuric acid (Schiff, *Deut. chem. Ges. Ber.*, vi. 26).

Phloroglucol reduces argentic nitrate, especially if ammonia be added, and also an alkaline cupric solution; it gives a deep violet-red coloration with ferric chloride. By the action of nitrous acid it is converted into *phloreïn*, $C_{12}H_8O_5$, which dissolves in alkalies forming a deep purple coloured solution (Benedikt, *Deut. chem. Ges. Ber.*, vii. 445). When dilute solutions of phloroglucol and of aniline or toluidine nitrate are mixed, and a solution of potassic nitrate is added, the liquid which is at first clear becomes after a time turbid and of a brownish-yellow colour, then orange-red, and finally a vermilion-red precipitate is produced (Weselsky, *ibid.*, ix. 216). This reaction affords an extremely delicate test for phloroglucol.

Constitution of pyrogallol and phloroglucol.—Although at present no direct proof of the constitution of these compounds can be advanced, there is little doubt that their relation to benzene may be expressed in the following manner:



Pyrogallol or metatrioxybenzene.



Phloroglucol or paratrioxybenzene.

Perhaps the most conclusive evidence in favour of the assumption that pyrogallol is metatrioxybenzene is derived from its behaviour on oxidation, whereby it is converted into a quinone derivative. This conclusion is also in accordance with its formation from gallic acid (q.v.), and from parachlorophenolorthosulphonic acid (p. 548), although on account of the frequent occurrence of isomeric change on fusing compounds with potassic hydrate, no great weight can be attached to this evidence. No proof has yet been given even that phloroglucol is derived from benezene, but Körner (*Gazetta chimica italiana*, 1874, iv. 425), incidentally refers to the formation of phloroglucol derivatives from the nitro-derivatives of paratribromobenzene, and the entire behaviour of phloroglucol is in accordance with the assumption that it is paratrioxybenzene. Its conversion into dichloracetic acid by the action of chlorine in presence of water is obviously analogous to that of the para-modification of trimethylbenzene,—mesitylene, into acetic acid on oxidation (p. 288), and may be regarded as evidence that it is a member of the same series of derivatives as mesitylene.

(1536) *Dimethylmetatrioxybenzene; Trioxymetaxylene:* $C_6H(CH_3)_2(OH)_3$.—This compound is obtained by the action of a warm aqueous solution of sulphurous acid on oxymetaxyloquinone (q.v.), $C_6H(CH_3)_2(OH)O_2$. It separates from an aqueous solution in large tabular crystals, containing a molecule of water of crystallization, which is expelled by heating to 80° (176° F.); the hydrated substance melts at 89° (192°·2 F.), but when anhydrous it melts at 122° (251°·6 F.). It is moderately soluble in cold, and very soluble in hot water; oxidizing agents very readily reconvert it into the quinone, and on allowing the aqueous solution to evaporate spontaneously the dark coloured quinhydrone is formed. When distilled over heated zinc dust it is reduced to metaxylene, $C_6H_4(CH_3)_2$. Acetic chloride converts it into the diacetate $C_6H(CH_3)_2(C_2H_3O_2)_3$, which crystallizes from alcohol in large glistening prisms, insoluble in water, but very soluble in hot alcohol; it melts at 99° (210°·2 F.). (Fittig and Siepermann, *Ann. Chem. Pharm.*, clxxx. 37).

(1537) *Phenylglycerol:* $C_6H_5.CH(OH).CH(OH).CH_2(OH)$.—This alcohol is obtained by heating the bromide formed by combining cinnamic alcohol with bromine (p. 395) with water and argentic acetate in open vessels for forty-eight hours; the solution freed from silver by sulphuretted hydrogen, concentrated, and then exposed in vacuo over sulphuric acid leaves the phenylglycerol as a pale yellow gummy mass, excessively soluble in water and alcohol, of a distinct bitter taste (Grimaux, *Compt. Rend.*, lxxvi. 1598).

(1538) *Propylmethylmetatrioxybenzene:* $C_3H_7{}^a.C_6H(CH_3)(OH)_3$.—This *trioxycymene* appears to be formed on treating oxythymoquinone with tin and hydrochloric acid; it is very readily reconverted into the oxyquinone on exposure of its solution to the air (Carstanjen, *Journ. pr. Chem.* [2], iii. 61).

(1539) *Trioxynaphthalene:* $C_{10}H_5(OH)_3$, is formed in a similar manner from oxynaphthaquinone (q.v.); it crystallizes in yellow needles, less soluble in water than in alcohol or ether. It is very readily oxidized, and therefore acts as a powerful reducing agent; an alkaline solution becomes red on exposure to the air, absorbing oxygen, the metallic derivative of the oxyquinone being formed (comp. p. 499; Graebe and Ludwig, *Ann. Chem. Pharm.*, cliv. 324).

§ XI. TETRAHYDRIC ALCOHOLS.—ALCOHOLS OF THE $C_nH_{2n-2}(OH)_4$ SERIES.

At present only two tetrahydric alcohols are known—viz., erythrol or erythrite, the tetrahydroxyl derivative of the paraffin normal tetrane, and naphtherythrol, $C_{10}H_8(OH)_4$.

(1540) ERYTHROL or ERYTHRITE; *Erythromannite* or *Phycite*: $C_4H_6(OH)_4$ or $CH_2(OH).CH(OH).CH(OH).CH_2(OH)$.—This substance exists ready formed in the alga *protococcus vulgaris*, and may also be obtained from the orsellinates of erythrite, picroerythrin or erythrin, the latter of which occurs in some species of orchella weed, such as *Roccella tinctoria* and *R. fuciformis*.

It is prepared from erythrin by boiling it with water and excess of lime in the manner already described when treating of the preparation of orcin (p. 528). After the solution has been neutralized and evaporated to dryness at 100° (212° F.), the solid mixture of orcin and erythrite is broken up and treated with strong alcohol, which readily dissolves the orcin, but leaves the erythrite, the latter being but slightly soluble in alcohol. The impure erythrite can readily be obtained pure and colourless by two or three crystallizations from boiling water, with the addition of some animal charcoal.

It crystallizes in large colourless quadratic prisms, which are insoluble in ether, but dissolve very readily in water, and sparingly in cold alcohol; it melts at 120° (248° F.), but cannot be distilled without undergoing decomposition; erythrol does not reduce alkaline solutions of cupric salts, and is not fermentable by yeast. It possesses but a feebly sweet taste. It is dissolved by concentrated nitric acid, being converted into the nitrate $C_4H_6(NO_3)_4$, which may be separated by the addition of concentrated sulphuric acid, and purified by washing with cold water, and crystallization from alcohol; it forms large shining colourless laminæ, which melt at 61° (141°·8 F.), and detonate by percussion or when heated. When treated with ammonic sulphide, erythrol is regenerated. By heating erythrol with concentrated hydrochloric or hydrobromic acid to 100—110° (212°—230° F.), it is converted into the compounds $C_4H_6Cl_2(OH)_2$ and $C_4H_6Br_2(OH)_2$. The dichlorhydrin forms colourless crystals, very soluble in water, which melt at 145° (293° F.) (De Luynes); on treatment with a mixture of concentrated nitric and sulphuric acids it yields the dinitrate $C_4H_6Cl_2(NO_3)_2$, which melts at 60° (140° F.), and has properties similar to those of the dinitrate derived from the dibromhydrin. The dibromhydrin is stated to be insoluble in water; it melts at 130° (266° F.). The dinitrate $C_4H_6Br_2(NO_3)_2$ is insoluble in water, but crystallizes from alcohol in long white needles, melting at 75° (167° F.); it does not detonate when struck (Champion, *Compt. Rend.*, lxxiii. 114).

When erythrol is distilled with a concentrated solution of hydriodic acid, it is converted into γ-iodotetrane or secondary butylic iodide, $CH_3.CHI.C_2H_5$.

By exposing a dilute aqueous solution to air in contact with platinum black, erythritic acid, $CH_2(OH).CH(OH).CH(OH).COOH$, is produced. When heated with potassic hydrate at about 240° (464° F.), erythrol furnishes potassic oxalate and acetate with evolution of hydrogen.

On distilling erythrol with formic acid it undergoes a decomposition similar to that of glycerin, the monoformin which is first produced being converted into water, carbonic anhydride, and a glycol of the formula $C_4H_6(OH)_2$, which at present is the only representative of the $C_nH_{2n-2}(OH)_2$ series. This glycol is a colourless thick liquid, soluble in water, and boils at about 200° (392° F.); it combines directly with bromine; its diacetate boils at about 202° (395°·6 F.) (Henninger, *Deut. chem. Ges. Ber.*, v. 1059; comp. p. 219).

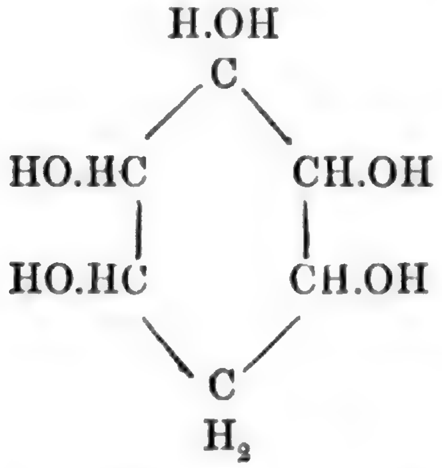
(1541) NAPHTHERYTHROL; *Naphthalene Alcohol:* $C_{10}H_8(OH)_4$.—This alcohol is obtained by warming a solution of the compound $C_{10}H_8Cl_2(OH)_2$, formed by the combination of naphthalene with hypochlorous acid, with potassic hydrate, and extracting by ether. It crystallizes in prisms, which rapidly turn brown; and decomposes when distilled. It is only slightly soluble in water, but easily in alcohol and ether, and dissolves with brown colour in an aqueous solution of potassic hydrate. It furnishes metallic derivatives when silver or lead salts, &c., are added to the alcoholic solution mixed with a little ammonia. It is stated that the solution of the alcohol in warm very dilute nitric acid leaves on evaporation yellow prisms of an acid of the composition $C_{10}H_8O_6$ (Neuhoff, *Ann. Chem. Pharm.*, cxxxvi. 342).

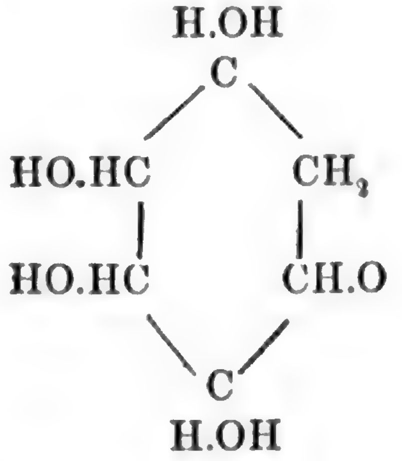
§ XII. PENTAHYDRIC ALCOHOLS OF THE $C_nH_{2n-3}(OH)_5$ SERIES.

Quercite, $C_6H_{12}O_5$, has been shown to be a pentahydric alcohol, and it is not improbable that pinite, and the so-called isodulcite, which are isomeric with quercite, are also pentahydric alcohols.

(1542) QUERCITOL OR QUERCITE: $C_6H_7(OH)_5$.—This substance is contained in acorns; to prepare it, the aqueous extract of bruised acorns is freed from dissolved tannic acid by heating it with lime, the filtrate is left to ferment with yeast to remove sugar, and the filtered liquid is then evaporated to a syrup, the crystals which separate after a time being recrystallized from water or from weak alcohol. Quercitol forms hard monoclinic prisms, sweet to the taste; it does not alter even at 215° (419° F.), but melts at 235° (455° F.) When heated with an excess of acetic anhydride to 100°—120° (212—248° F.) it is converted into the pentacetate $C_6H_7(C_2H_3O_2)_5$; acetic chloride is without action at its boiling point, but also converts the alcohol into the pentacetate when heated with it in closed vessels to 100° (212° F.). Di- and tetracetates may be obtained by the action of limited quantities of the anhydride. These acetates are all extremely hygroscopic; the pentacetate melts at 37°—43° (98°·6—109°·4 F.). On treatment with a mixture of concentrated nitric and sulphuric acids, quercitol is converted into the pentanitrate $C_6H_7(NO_3)_5$. A concentrated solution of hydrochloric acid is entirely without action on quercitol even at 100° (212° F.). On oxidation with dilute nitric acid, or with bromine and water, it appears to furnish only oxalic acid and carbonic anhydride (Homann, *Deut. chem. Ges. Ber.*, viii. 1039; and *Dissertation*, Würzburg).

Most remarkable, however, is the behaviour of quercitol with hydriodic acid, which reduces it to benzene (Prunier, *Compt. Rend.*, lxxxii. 1113). From this it is probable that the constitution of quercitol is represented by one of the following formulæ:





(1543) ***Pinite:*** $C_6H_{12}O_5$.—Pinite is a crystalline substance contained in the sap of the *Pinus lambertiana* of California. It is deposited from the aqueous extract of the hardened juice in hard white nodules. It melts above 150° (302° F.), is very soluble in water, slightly in alcohol, and has a very sweet taste; like quercitol it is not fermentable, and does not reduce an alkaline cupric solution. It is an optically active substance, its rotatory power, according to Berthelot, being $[a]_j = +58°·6$. In its general behaviour it appears closely to resemble quercitol, and like the latter is a body of considerable stability, but scarcely anything is known of its derivatives.

(1544) *Isodulcite:* $C_6H_{12}O_6 + OH_2$.—This body is produced by the decomposition of quercitrin, a substance contained in quercitron bark, under the influence of acids. It crystallizes with great facility in large well-formed crystals resembling those of cane sugar, sweet to the taste, and very soluble in water; the solution is dextrorotatory. It melts with loss of water between 105° and 110° (221° and 230° F.).* Isodulcite reduces an alkaline cupric solution, its reducing power being almost equal to that of grape sugar; it is not fermentable. On treatment with a mixture of concentrated nitric and sulphuric acids, it is converted into a nitrate of the composition $C_6H_9O_2(NO_3)_3$ (Hlasiwetz and Pfaundler, *Ann. Chem. Pharm.*, cxxvii. 362). When oxidized with nitric acid it yields a dibasic acid, *isodulcitic acid*, $C_6H_{10}O_9$ (Malin, *ibid.*, cxlv. 197).

§ XIII. HEXAHYDRIC ALCOHOLS.—ALCOHOLS OF THE $C_nH_{2n-4}(OH)_6$ SERIES.

The only hexahydric alcohols at present known besides mannite and dulcite—both of which apparently are hexhydroxyl derivatives of the paraffin normal hexane—are hexoxydiphenyl, $C_{12}H_4(OH)_6$; sorbite, and phenose, $C_6H_6(OH)_6$—a body of which, however, our knowledge is very imperfect. Inosite and dambose are perhaps also hexhydric alcohols.

(1545) MANNITOL OR MANNITE: $C_6H_8(OH)_6$.—This substance was discovered by Proust in 1806. It is the chief constituent of *manna*, the dried sap of *Fraxinus ornus*, but it also occurs, though in much smaller quantity, in many other plants, and in fungi. On exhausting manna with boiling alcohol, and allowing the solution to cool, it is deposited in small crystals which may be purified by recrystallization. Mannitol is formed by the action of sodium amalgam on the mixture of dextrose and lævulose, $C_6H_{12}O_6$, obtained on boiling a solution of cane sugar with a small quantity of sulphuric acid (Linnemann). Dewar has shown that dextrose may be converted into mannitol in this manner, and from his experiments it seems probable that it may also be formed from lævulose, for he found that, although the whole of the cane sugar was not obtained in the form of mannitol, a gummy uncrystallizable substance being simultaneously produced, the crude product was entirely without action on polarized light (*Phil. Mag.* [4], xxxix. 345).†

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* Löwe (*Zeits. anal. Chem.*, xiv. 233) finds, however, that quercitrin from quercitron bark is not a glucoside, but merely differs from quercetin by the elements of water; quercetin being the anhydride of quercitrin. It is difficult to reconcile this statement with the circumstantial account of isodulcite given by Hlasiwetz and Pfaundler, unless we suppose that the quercitron examined by them was really a different compound from Löwe's, and not identical.

† Mr. C. Haughton Gill informs us that he has obtained mannitol from lævulose prepared by Dubrunfant's method by treating its aqueous solution with sodium amalgam (comp. Bouchardat, *Ann. Ch. Phys.* [47], xxvii. 207), and Krusemann (*Deut. chem. Ges. Ber.*, ix. 1465) has recently prepared it in a similar manner from lævulose from inulin.—[EDS.]

Mannitol crystallizes in thin four-sided rhombic prisms, soluble in about 6½ pts. of water at ordinary temperatures; it melts between 160° and 165° (320°—329° F.); at about 200° (392° F.) it begins to boil, and may be distilled with very little decomposition even at the ordinary atmospheric pressure. It exerts but a feeble lævorotatory action on polarized light, the deviation produced by a 15 per cent. solution, in a tube three metres long, being 0° 15′ (Bouchardat, *Compt. Rend.*, lxxx. 120). It is only slightly sweet to the taste, and does not reduce an alkaline cupric solution; it slowly ferments in contact with ordinary beer yeast (Muntz, *Ann. Chem. Phys.* [5], viii. 80).

On treatment with a mixture of concentrated nitric and sulphuric acids, mannitol is converted into the hexanitrate $C_6H_8(NO_3)_6$. It forms white acicular crystals, insoluble in water, but soluble in alcohol or ether, and which melt at 108° (226°·4 F.); it explodes violently on being struck. By the action of ammonic sulphide and other reducing agents, it is reconverted into mannitol. The corresponding acetate $C_6H_8(C_2H_3O_2)_6$, is obtained by heating mannitol in an open vessel with a considerable excess of acetic anhydride, and crystallizes from its solution in the latter in prisms which melt at 119° (246°·2 F.).

By heating mannitol at 100° (212° F.) for ten hours, with fifteen times its weight of a solution of hydrochloric acid saturated at 0° (32° F.), it is converted into the dichlorhydrin $C_6H_8Cl_2(OH)_4$; the corresponding dibromhydrin is prepared in a similar manner, the mannitol and hydrobromic acid being heated together for two hours only. Both crystallize in colourless plates; the former melts at 174° (345°·2 F.), and dissolves in 22 parts of water at 14° (57°·2 F.); the latter melts at 178° (352°·4 F.), and is insoluble in cold but dissolves in warm water. On treatment with a mixture of nitric and sulphuric acids, they are converted into the nitrates $C_6H_8Cl_2(NO_3)_4$ and $C_6H_8Br_2(NO_3)_4$, both of which are insoluble in water, but soluble in alcohol, and crystallize in needles; the former melts at 145° (293° F.) (Bouchardat, *ibid.*, lxxv. 1187; lxxvi. 1550).

All these derivatives are optically active; the specific rotatory powers of their solutions, according to Bouchardat, are as follows:

Mannitol hexacetate $[\alpha]_D = +\ 18°$
„ hexanitrate $[\alpha]_D = +\ 42°{\cdot}2$
„ dichlorhydrin $[\alpha]_D = -\ 3°{\cdot}7$

On distilling mannitol with a concentrated solution of hydriodic acid, it is converted into normal secondary hexylic iodide, $CH_3.CHI.CH_2.CH_2.CH_2.CH_3$ (Erlenmeyer and Wanklyn):

$$\underset{\text{Mannitol.}}{C_6H_8(OH)_6} + 11HI = \underset{\text{Hexylic iodide.}}{C_6H_{13}I} + 6OH_2 + 5I_2.$$

On oxidizing mannite under the influence of platinum black—by exposing to the air a mixture of the two substances moistened with water—mannitic acid $C_6H_{12}O_7$ or $C_5H_6(OH)_5.COOH$, is produced; when, however, mannite is oxidized with nitric acid it is converted into saccharic acid, $C_4H_4(OH)_4(COOH)_2$.

(1546) Dulcitol or Dulcite; *Melampyrite:* $C_6H_8(OH)_6$.—This isomeride of mannitol is the chief constituent of the so-called dulcite manna from Madagascar, and may be obtained in a pure state by crystallization from boiling water; it occurs in the sap of *Melampyrum nemorosum*, and of many other plants. It is produced together with mannitol on treating a solution of milk sugar, or of milk sugar "inverted" by boiling with a small quantity of sulphuric acid, with sodium amalgam, being formed in the latter case by the hydrogenation of α-lactose (q.v.) (Bouchardat, *Ann. Ch. Phys.* [4], xxvii. 75, 101).

Dulcitol crystallizes in hard monoclinic prisms, scarcely sweet to the taste; it melts at about 188° (370°·4 F.), and is decomposed on distillation. It is much less soluble in water than mannitol, and is but slightly soluble even in boiling alcohol; it does not reduce an alkaline cupric solution. Its solution has no appreciable action on polarized light, and apparently none of its derivatives are in a marked degree optically active. Like mannitol, its solution is not coloured when warmed with an alkali, and it is not carbonized by sulphuric acid, this acid apparently converting both mannitol and dulcitol into acid sulphates.

A mixture of concentrated nitric and sulphuric acids converts dulcitol into the hexanitrate $C_6H_8(NO_3)_6$, which crystallizes from alcohol in colourless needless; it melts at about 70° (158° F.). The hexacetate, $C_6H_8(C_2H_3O_2)_6$, obtained by the action of acetic anhydride at 180° (356° F.), crystallizes in plates fusible at 171° (339°·8 F.). The hexabenzoate $C_6H_8(C_7H_5O_2)_6$, formed by heating dulcitol with benzoic chloride to 150° (302° F.), melts at 147° (296°·6 F.); it is quite insoluble in water, and only slightly soluble in alcohol.

Dulcitol dissolves easily in a saturated solution of hydrochloric acid, and on standing separates from the solution in crystals of the composition $C_6H_{14}O_6.HCl + 3H_2O$; this compound can exist only in an atmosphere saturated with hydrochloric acid. Corresponding compounds with hydrobromic and hydriodic acid may be obtained. Mannitol does not exhibit a similar tendency to combine with acids. By heating dulcitol with hydrochloric acid, it is converted into the dichlorhydrin $C_6H_8Cl_2(OH)_4$, which is insoluble in cold water, and is decomposed by hot water; it melts at 180° (356° F.), but like the mannitol derivative is decomposed (Bouchardat, *lot. cit.*, p. 145). The dibromhydrin is in all respects a similar compound, but decomposes more readily. By the action of a mixture of concentrated nitric and sulphuric acids on the dichlorhydrin and dibromhydrin of dulcitol, the tetranitrates $C_6H_8Cl_2(NO_3)_4$ and $C_6H_8Br_2(NO_3)_4$ are obtained; they are soluble in alcohol and melt respectively at 108° (226°·4 F.) and 110 (230° F.)

On distilling dulcitol with a concentrated solution of hydriodic acid, it furnishes a hexylic iodide which is in all respects identical with that from mannitol (Hecht, *Ann. Chem. Pharm.*, clxv. 146).

Dulcitol is converted by oxidation with nitric acid into mucic acid, $C_6H_{10}O_8$, which is isomeric with saccharic acid.

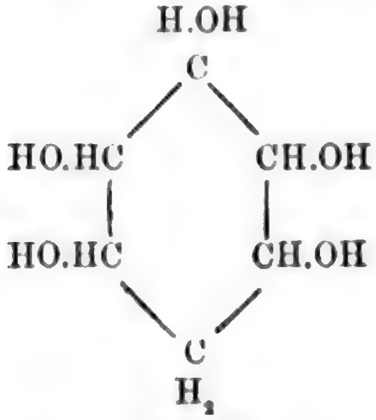
The constitution of mannitol and dulcitol, like that of hydrobenzoin and isohydrobenzoin, is at present involved in obscurity. The difference in their behaviour on oxidation, in their physical properties, and in the physical properties of their derivatives is so great, that it appears in the highest degree probable that they are bodies of different chemical constitution. From their behaviour on treatment with hydriodic acid, we must regard them as derivatives of the same paraffin, normal hexane, and on account of their stability we must suppose that each of the six hydroxyl groups is associated with a different carbon atom; but normal hexane can only furnish a single hexhydric alcohol in which each of the OH groups is attached to a different carbon atom, viz.:

$CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$	$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH_2(OH)$.
Normal hexane.	? Mannitol and Dulcitol.

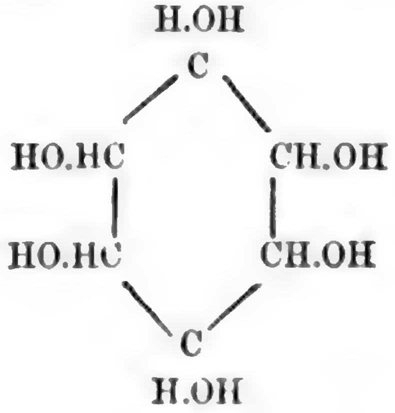
(1547) **Sorbite**: $C_6H_{14}O_6$.—This substance is obtained from the expressed juice of mountain ash berries. It separates from water in nacreous crystals of the composition $2C_6H_{14}O_6 + OH_2$, which become anhydrous when heated above 100° (212° F.). The hydrated compound melts at 102° (215°·6 F.), and the anhydrous substance at 110° (230° F.). It is inactive to polarized light, and does not reduce an alkaline cupric solution. Like mannitol and dulcitol it is not carbonized by concentrated sulphuric acid; it is not fermentable (Boussingault, *Compt. Rend.*, lxxiv. 939).

(1548) **Phenose**: (?) $C_6H_6(OH)_6$.—Benzene combines directly with hypochlorous acid forming the trichlorhydrin, $C_6H_6Cl_3(OH)_3$, and, according to Carius, by carefully warming a dilute aqueous solution of this compound with sodic carbonate, it is converted into the hexhydric alcohol $C_6H_6(OH)_6$ (*Ann. Chem. Pharm.*, cxxxvi. 326). The preparation of phenose in this manner is attended with great difficulty, however, both on account of the readiness with which the trichlorhydrin undergoes oxidation by the hypochlorous acid, and also from the extreme alterability of the alcohol itself. On this account, phenose has been but very imperfectly investigated, and even its composition can scarcely be said to be satisfactorily established. It is described by Carius as an amorphous deliquescent substance, easily soluble in water and alcohol, its taste being sweet at first, but afterwards sharp. It is decomposed when heated a little above 100° (212° F.), emitting a caramel-like odour, and when submitted to dry distillation it furnishes a distillate containing acetic acid. It is rapidly converted into humus-like substances when heated with dilute acids or alkalies. On warming with even very dilute nitric acid, it is oxidized to oxalic acid. It readily reduces alkaline solutions of cupric salts. When distilled with a solution of hydriodic acid it is chiefly carbonized, but a small quantity of a hexylic iodide is formed; this iodide is more readily produced by heating the trichlorhydrin $C_6H_6Cl_3(OH)_3$ with hydriodic acid, and is apparently identical with the hexylic iodide from mannite.

The difference between quercitol and phenose in stability, and in their behaviour with hydriodic acid, is remarkable, for if the latter be really the alcohol of the composition $C_6H_6(OH)_6$,* from the manner in which it is formed, we might expect that its constitution would be very similar to that we have attributed to quercitol, viz.:



Quercitol.



Phenose.

but it appears not improbable that inosite, and not phenose, is the analogue of quercitol.

(1549) Inosol; *Inosite* or *Phaseomannite*: $C_6H_{12}O_6$ or (?) $C_6H_6(OH)_6$.—Inosite was discovered by Scheerer in 1850 in the muscular substance of the heart. It has since been found to exist in the brain, kidney, liver, lungs, and spleen; in horseflesh; and in human kidneys, and in the urine in cases of albuminuria. It is present in considerable quantity in cochineal (Hugo Müller, *private communication*). It has also been obtained from a number of plants: for example, from the unripe seeds of the French or kidney bean (***Phaseolus vulgaris***); from the green pods and unripe seeds of the garden pea (***Pisum sativum***); from the heads of the common cabbage; and from grape juice (Hilger, *Ann. Chem. Pharm.*, clx. 333).

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* Kekulé (*Lehrbuch*, iii. p. 162) is inclined to regard phenose as the hydrate of a trihydroxylbenzene $-C_6H_3(OH)_3,3OH_2$, formed from the trichlorhydrin $C_6H_6Cl_3(OH)_3$ by the abstraction of the elements of three molecules of hydrochloric acid, in the same way that metatrichlorobenzene is formed from the chloride $C_6H_6Cl_6$. As it is not identical with either pyrogallol or phloroglucol, it could only be the trihydroxyl-benzene in which the three OH groups are contiguous (see p. 552); the formation of a compound of this constitution by such a reaction appears to be somewhat improbable, however.

It is best prepared from unripe beans, which contain about three-quarters per cent. of their weight of inosite (Vohl). The finely shredded beans are placed in a pressing bag, which is immersed in boiling water or steamed for half an hour, and then strongly pressed; the aqueous extract and the expressed liquor are evaporated to a syrup on the water bath, alcohol is then added until a permanent turbidity is produced, and the crystals which form are purified by repeated crystallization from water with the aid of animal charcoal.

When pure, inosite crystallizes in large well-formed monoclinic prisms from an aqueous solution left to evaporate spontaneously, but if impure it separates in cauliflower-like masses. The crystals contain two molecules of water, and effloresce in dry air; they dissolve in about six parts of water at 19° (66°·2 F.), but are insoluble in anhydrous alcohol or ether. The aqueous solution is not precipitated by plumbic acetate, but basic plumbic acetate produces a white precipitate which apparently has the composition $C_6H_6(OH)_4(O.PbOH)_2$. Anhydrous inosite melts at about 210° (410° F.); at higher temperatures it is decomposed. Inosite has a sweet taste, but is not optically active, and does not reduce an alkaline cupric solution; it does not ferment in contact with beer yeast, but when mixed with decaying cheese and chalk, it undergoes the lactic fermentation (Vohl, *Deut. chem. Ges. Ber.*, ix. 984). It is not altered by boiling either with a concentrated solution of potassic hydrate, or with dilute hydrochloric or sulphuric acid, and is not blackened by sulphuric acid even at 100° (212° F.). If it is evaporated to dryness with dilute nitric acid, no action takes place until the acid becomes moderately concentrated, when nitrous fumes are freely evolved; the residue contains oxalic acid, and on dissolving it in water, neutralizing with calcic carbonate, and separating the calcic oxalate by filtration, a solution is obtained from which (? on evaporation) a purple-red flocculent mass separates after some time: this substance is soluble in dilute acids, and may be reprecipitated from the acid solution by ammonia, apparently unchanged. Scheerer's test for inosite, which consists in evaporating it nearly to dryness with aqueous nitric acid, then adding ammonia and a small quantity of calcic chloride solution, and again evaporating, when a rose-red coloration is produced, doubtless depends on the formation of this substance, which probably is a product of the action of nitrous acid. Nitric acid of sp. gr. 1·52, even if boiling, does not oxidize inosite, but converts it into a substance which, according to Vohl's analysis (*Ann. Pharm. Chem.*, cv. 332), would appear to be the hexanitrate $C_6H_6(NO_3)_6$; it is insoluble in water, but easily soluble in alcohol, crystallizing from the latter in rhombohedrons. The formation of this compound is at present the only evidence we have to show that inosite is a hexhydric alcohol. Inosite is not reduced on distillation with a saturated solution of hydriodic acid; but when heated with bromine and water at 100° (212° F.), it is slowly oxidized, much carbonic anhydride being evolved (H. Müller, *private communication*).

Inosite, it will be evident, is a body of remarkable stability, and in this respect closely resembles quercitol; indeed it appears highly probable, as we have above pointed out, that, like the latter, it is derived from a hydrocarbon C_6H_{12} in which the carbon atoms are united in a closed chain.

(1550) DAMBOSE.—This compound is obtained on heating dambonite or bornesite to 100° (212° F.) with hydriodic acid solution (Girard, *Compt. Rend.*, lxvii. 820; lxxiii. 426). Dambonite occurs in small quantity in a peculiar kind of caoutchouc exported from the French colony of Gaboon on the west coast of Africa, and bornesite in Borneo caoutchouc; these two kinds of caoutchouc being apparently the produce of climbing plants of the genus *urceola*.

Dambose, $C_6H_{12}O_6$, is easily soluble in water, from which it crystallizes in rather thick anhydrous prisms, whereby it is distinguished from inosite, which it resembles in other respects. It is a very stable substance, melting at 230° (446° F.)

without undergoing decomposition. Bromine is without action on it at 160° (320° F.), but at 180° (356° F.) hydrobromic acid is evolved and a substitution product is formed. It is optically inactive, and does not ferment with yeast.

Bornesite, $C_7H_{14}O_6$, is a crystalline substance very soluble in water, which melts at 175° (347° F.). It is optically active, having the specific rotatory power $[\alpha]_D = +32°$. It does not reduce an alkaline cupric solution, but acquires this property on being boiled with slightly acidulated water.

Dambonite, $C_8H_{16}O_6$, is also crystalline and easily soluble in water, but like bornesite only sparingly in alcohol; it melts at 190° (374° F.), and when cautiously heated, sublimes at 200°—210° (392°—410° F.) without decomposition in long slender shining needles. It is optically inactive, and does not reduce an alkaline cupric solution; dilute sulphuric acid does not act upon it. Dambonite forms with potassic iodide a crystalline compound of the composition $C_8H_{16}O_6KI$.

From their behaviour with hydriodic acid, bornesite and dambonite must be regarded respectively as the mono- and dimethyl derivatives of dambose; at present, however, there is no evidence to show what is the nature of dambose, and even its molecular formula is not yet established.

(1551) HEXOXYDIPHENYL : $C_6H_2(OH)_3.C_6H_2(OH)_3$.—This compound is obtained by heating hydrocœrulignone with hydrochloric acid:

$$C_{12}H_4(OH)_2(OCH_3)_4 \quad + \quad 4HCl \quad = \quad C_{12}H_4(OH)_6 \quad + \quad 4CH_3Cl.$$

It forms colourless, glistening, extremely thin plates, and is soluble in most solvents. It dissolves in alkalies forming a magnificent violet-blue coloured solution, which is doubtless the result of oxidation. When distilled over heated zinc dust, it is reduced to diphenyl, $C_{12}H_{10}$. The hexacetate $C_{12}H_4(C_2H_3O_2)_6$, formed from it by the action of acetic anhydride, crystallizes in prisms, and melts at 145° (293° F.) (Liebermann, *Ann. Chem. Pharm.*, clxix. 241).

APPENDIX TO (1448).—Two tertiary heptylic alcohols containing *three* dissimilar radicles have recently been obtained, viz., *propylethylmethylcarbinol*, $C_3H_7{}^{\alpha}C(C_2H_5)(CH_3).OH$, and its isomeride, *isopropylethylmethylcarbinol*, $C_3H_7{}^{\beta}C(C_2H_5)(CH_3).OH$: the former by the addition, first, of a molecular proportion of zincic methide to a molecular proportion of butyric chloride, $C_3H_7{}^{\alpha}.COCl$, and then of a molecular proportion of zincic ethide, and after some time treating the product with water; and the latter in a similar manner from isobutyric chloride, $C_3H_7{}^{\beta}.COCl$. Propylethylmethylcarbinol boils at 135°—138° (275°—280°·4 F.); its iodide furnishes a heptylene (?) $C_2H_5.CH{=}C(CH_3)(C_2H_5)$, which boils at 90°—95° (194°—203° F.). Isopropylethylmethylcarbinol boils at 124°—127° (255°·2—260°·6 F.); the heptylene (?) $(CH_3)_2C{=}C(CH_3)(C_2H_5)$, from its iodide boils at 75°—80° (167°—176° F.) (Pawlow, *Deut. chem. Ges. Ber.*, ix. 1311).

APPENDIX TO (1522).—By heating naphthalene tetrachloride (1367), $C_{10}H_8Cl_4$, with 30 pts. of water for some hours to 180°—190° (356°—374° F.), it is converted into the dihydric alcohol $C_{10}H_8Cl_2(OH)_2$, which crystallizes in large ill-defined prisms. The diacetate derived from it melts at 130° (266° F.). When distilled with concentrated hydrochloric acid it furnishes a monochloronaphthol, $C_{10}H_6Cl.OH$, melting at 109° (228°·2 F.) (Grimaux, *Bull. Soc. Chem.* [2], xviii. 205; *Compt. Rend.*, lxxvi. 575).

General Review of the Alcohols.

(1552) The comparison of the alcohols of various series is of interest in many respects; at present, however, on account of our limited knowledge of all but those derived from the paraffins and the hydrocarbons of the benzene series, it is attended with even greater difficulties than that of the hydrocarbons of various series.

The displacement of hydrogen in hydrocarbons by the group OH appears, in all cases, to lead to the production of less volatile compounds: for example, ethane is gaseous, ethylic alcohol is a mobile liquid which boils at about 78° C., and glycol is a syrupy liquid boiling at 197° C.; again, propane is gaseous, propylic alcohol is a mobile liquid and boils at about 97° C., propylene glycol is a syrupy liquid and boils at 216° C., and glycerin which is very viscid boils at about 280° C. under the ordinary atmospheric pressure; lastly, benzene is a mobile liquid and boils at 81° C., whilst phenol is a crystalline solid and boils at 184° C. Apparently, however, the diminution in volatility is not directly proportional to the number of hydroxyl groups introduced: those first introduced usually having the greatest influence.

As in the case of isologous hydrocarbons, the boiling points of isologous alcohols are generally higher the less hydrogen they contain, with the exception of propylic and allylic alcohols, which have approximately the same boiling point. The same relation obtains between most of the propylic and allylic compounds corresponding in composition; the specific gravity of allylic alcohol, however, is considerably higher than that of propylic alcohol.

The displacement of hydrogen in hydrocarbons by the group OH always causes a considerable increase in specific gravity: thus, whereas normal tetrane has the specific gravity ·600, the specific gravity of normal primary butylic alcohol is ·824, and that of erythrol 1·59.

The lower monohydric alcohols derived from the paraffins possess characteristic odours and a burning taste, but the polyhydric alcohols derived from these hydrocarbons are all odourless—doubtless on account of their volatility being but slight—and are mostly more or less sweet to the taste. The monohydric alcohols derived from the hydrocarbons of the benzene series also possess characteristic odours, which is probably in a measure accounted for by the fact that, although bodies of high boiling point, they are all very volatile; the polyhydric alcohols derived from these hydrocarbons are odourless. The alcohols of different degrees of hydricity and of the various isologous series, and even those of the same homologous series, appear to differ remarkably in their physiological action. In the case of the alcohols of the ethylic series, the activity increases at first with the increase of molecular weight, and from experiments on dogs, Dujardin, Beaumetz, and Audigé (*Compt. Rend.*, lxxxiii. 80) find that the lethal dose of propylic alcohol is about one-half, of isoprimary butylic alcohol about one-third, and of fermentation amylic alcohol only about one-third as great as that of ethylic alcohol. Methylic alcohol is somewhat more active than ethylic alcohol. Heptylic alcohol (? normal primary) and octylic alcohol (? from castor-oil), however, in the pure state are only about as active as ethylic alcohol, but when diluted to ten times their bulk with the latter alcohol they are fatal to about the same extent as butylic alcohol. Cetylic alcohol, which is insoluble both in water and alcohol at the ordinary temperature, is inert. Phenol and its homologues, which are especially characterized by the readiness with which they effect the coagulation of albumen, are much more poisonous than the alcohols of the ethylic series, the effect of phenol on animals being to cause great dilatation of the blood-vessels, weak respiration, and lowering of temperature. The polyhydric alcohols are apparently much less active than the monohydric; few observations, however, have been made on this point.

The alcohols, especially those containing several hydroxyl groups, are much less stable compounds than the corresponding hydrocarbons, and are much more readily acted on by reagents generally.

Ethylic alcohol and its homologues, like the paraffins, do not form additive compounds with chlorine or bromine, whilst allylic and propargylic alcohols, like the hydrocarbons of the ethylene and acetylene series, combine respectively with two and four atoms of bromine, forming substitution derivatives of the corresponding alcohols of the ethylic series; the phenols and alcohols of the benzylic series, however, and the isologous alcohols containing relatively less hydrogen, do not under any conditions appear to form additive compounds which are of sufficient stability to permit of their isolation. There is reason to believe, at least in some cases, that the formation of substitution derivatives of the phenols, &c., is preceded by that of highly unstable additive compounds; at present, however, there is no evidence to show that this is always the case.

In their behaviour with nitric acid, and with sulphuric acid, and also on oxidation, the alcohols bear considerable resemblance to the hydrocarbons from which they are derived. Thus, the alcohols of various degrees of hydricity derived from the paraffins, or which may be regarded as formed from the alcohols derived from the paraffins by the displacement of one or more of the hydrogen atoms in the hydrocarbon radicles of these alcohols by radicles such as phenyl, C_6H_5, &c., are either converted into normal or basic ethereal salts, or oxidized, by the action of nitric acid, and yield acid ethereal salts on treatment with sulphuric acid; whereas the phenols, naphthols, orcinols, &c., furnish nitro-substitution derivatives when submitted to the action of nitric acid, and sulpho-acids on treatment with sulphuric acid. It will be remembered also that by the action of the haloid acids on the alcohols of the former class, the OH groups are more or less readily displaced by halogens, the displacement seldom being perfect, however, in the case of polyhydric alcohols; the alcohols of the latter class are mostly unaffected by the haloid acids. It is possible, however, to displace the OH group by chlorine or bromine in most, if not all alcohols, by submitting them to the action of phosphoric pentachloride or pentabromide, although on account of the occurrence of secondary reaction, the isolation of the product of the primary reaction is often impossible, and, therefore, a compound is not always characterized as an alcohol by its behaviour with phosphoric pentachloride.

A method of distinguishing the alcohols generally from all other compounds is afforded by their behaviour with the acid anhydrides or chlorides, such as acetic and benzoic anhydrides and acetic and benzoic chlorides. By the action of these compounds on the alcohols, the hydrogen in the OH groups of the latter is more or less readily displaced by acid radicles, the displacement of the whole of the hydrogen present in this form being readily effected, if a sufficient excess of the reagent be employed, either on heating the materials together under the ordinary atmospheric pressure, or at a comparatively low temperature in closed tubes. In order, however, in this way to prove that a compound is an alcohol, it is necessary to introduce in place of hydrogen as many of the acid radicles as the compound contains oxygen atoms. Numerous instances of the formation of ethereal salts of this kind by the action of the acid chlorides or anhydrides, have been given in the foregoing description of the alcohols. On account of the formation of chlorinated compounds when the acid chlorides are employed, the acid anhydrides are frequently to be preferred for this purpose.

The behaviour of the alcohols of various series with alkalies is complementary to their behaviour with acids: those which form ethereal salts with acids, such as nitric or sulphuric acid, exhibiting but little tendency to form metallic derivatives stable in presence of water; whereas the phenols and other alcohols which do not form ethereal salts with these acids exhibit marked acid functions, furnishing metallic derivatives which are not readily, if at all, decomposed by water. But just as all alcohols exhibit basic functions—that is to say, are capable of being converted into ethereal salts by the displacement of the hydrogen in the OH group by negative radicles, so also they all exhibit acid functions and are capable of exchanging hydrogen for positive radicles. For example, although ethylic alcohol apparently is not acted upon by an aqueous solution of an alkali, double decomposition occurs when sodic hydrate is dissolved in it, a certain amount of the derivative $C_2H_5.ONa$ being formed; and it may be entirely converted into this compound by the action of metallic sodium, just as sodic hydrate, NaOH, is converted into sodic oxide, NaONa, when fused with sodium. Phenol, on the other hand, dissolves even in an aqueous solution of sodic hydrate, and is converted into sodium phenol, $C_6H_5.ONa$, which is fairly stable in presence of water, whereas the compound $C_2H_5.ONa$ is immediately decomposed by water. The most striking evidence of this is afforded by thermo-chemical investigation. Thus, according to Berthelot (*Compt. Rend.*, lxxiii. 663), there is no appreciable alteration of temperature on mixing dilute solutions of ethylic alcohol and potassic hydrate, which is an indication that no chemical action takes place. On mixing semi-normal solutions of glycerol and of sodic hydrate in the proportion of $(C_3H_8O_3 + Aq) : (NaOH + Aq)$, only 370 units of heat* are developed, and about the same amount of heat is absorbed on diluting the resulting mixture with water, so that it may be concluded that the sodium derivative formed in the first reaction is decomposed by the addition of water. From other experiments Berthelot finds: 1. That by the action of alkalies on glycerol an amount of heat is developed not exceeding in the case of semi-normal solutions about $\frac{1}{10}$ of that developed by the action of the acids on the alkalies. 2. That the heat developed increases with the number of molecular proportions of glycerol added to one molecular proportion of sodic hydrate, and *vice versâ*, but without being proportional to the quantities added, either of the one or the other compound. 3. That the compound formed in a concentrated solution is decomposed on the addition of a sufficient amount of water, since the heat developed diminishes as the dilution becomes greater. The behaviour of mannitol is similar: the amount of heat developed by the addition of successive quantities of a semi-normal solution of sodic hydrate to a semi-normal solution of mannitol being in one experiment as follows:

$$\begin{array}{lll} (C_6H_{14}O_6 + Aq) + \frac{1}{2}(NaOH + Aq) & \text{develop} & 690 \text{ units} \\ \qquad\qquad\qquad + \frac{1}{2}(NaOH + Aq) & \quad ,, & 370 \quad ,, \\ \qquad\qquad\qquad + \frac{1}{2}(NaOH + Aq) & \quad ,, & 150 \quad ,, \end{array}$$

On diluting the solution, slightly more heat was absorbed than had previously been developed, proving the decomposition of the compound formed in the more concentrated solution. In the case of phenol, however, it was found that the amount of heat developed was independent of the quantity of water present, phenol in this respect resembling the true acids, from which it differs by having only about half as great a heat of neutralization.† But the heat of neutralization of trinitrophenol—the so-called picric acid—according to Berthelot, is equal to that of the strongest acids; it will be remembered that it has already been pointed out that the nitrophenols exhibit more pronounced acid properties than the phenols themselves.

The behaviour of the alcohols of various series is thus obviously analogous to that of the hydroxides or hydrates of various elements; we may, in fact, compare the two great classes of alcohols, on the one hand, to the hydroxide of the positive element zinc, and on the other, to the hydroxide of the negative element chlorine: the hydrogen in zincic hydroxide, $Zn(OH)_2$, like that in ethylic alcohol, being readily displaced by acid radicles, but also by positive radicles as shown by the formation of compounds such as $Zn(OK)_2$; whereas the hydrogen in hypochlorous acid, HOCl, although most readily displaced by positive radicles may also be displaced by negative radicles, by the group C_2H_3O, for example, as in the salt chlorine acetate, $C_2H_3O.OCl$. It is just as impossible, however, strictly to divide the alcohols into two classes according to their behaviour with alkalies, as it is to divide the hydroxides derived from the various elements into the two classes of acids and bases.

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* A solution containing half a molecular proportion in grams of the substance per litre is termed a semi-normal solution. A unit of heat is the amount of heat required to raise the temperature of 1 gram of water from 0° to 1° C.

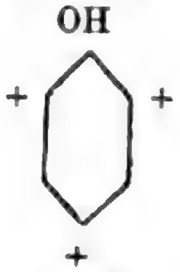
† On neutralizing solutions of a large number of the stronger acids by a solution of potassic or sodic hydrate, between 13,000 and 14,000 units of heat are developed for each molecular proportion in grams of alkali added.

All alcohols which, like phenol, are formed from hydrocarbons in which it may be supposed the carbon atoms are either entirely or partially united in a closed chain (p. 392) by the displacement by the group OH of hydrogen atoms attached to the carbon atoms which are a part of the closed chain, resemble phenol in their behaviour with alkalies; those, on the other hand, which are formed by the displacement of hydrogen atoms attached to carbon atoms which are part of an open chain resemble ethylic alcohol, glycerol, and mannitol. Hence it would appear, that all hydrocarbon radicles in which the carbon atoms are either wholly or partially united in a closed chain are more or less negative, whilst those in which the carbon atoms form an open chain are more or less positive.

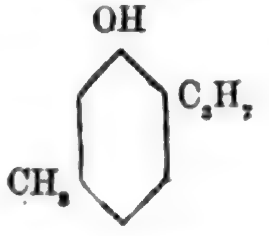
Phenol has apparently more marked acid functions than any other alcohol, for not only do its homologues exhibit acid functions to a less and less extent as they increase in molecular weight, but a similar alteration attends the increase in the number of loops in the chain of carbon atoms (comp. p. 394), the naphthols, for example, forming metallic derivatives which appear to be less stable than those of phenol. In the ethylic series of alcohols, the basic character is more and more evident as the series is ascended.

The behaviour of the alcohols on oxidation has already been discussed, and need not be again referred to. But attention may be directed to the difference in the result obtained by the employment of different oxidizing agents, a subject which has not yet by any means received the notice which it deserves. Especially remarkable is the action of agents such as chromic acid as compared with that of nitric acid on the alcohols of the ethylic series: the former reagent leading in the case of ethylic alcohol to the production of aldehyde and acetic acid, whereas this alcohol is converted by the action of the latter reagent into glycolic acid, &c., the CH_3 group being unaffected in the one case, but having its hydrogen displaced by OH in the other.

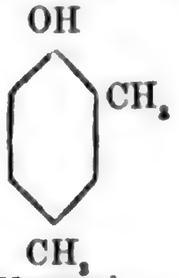
The formation of substitution derivatives from the alcohols of various series by the action of chlorine, &c., is apparently subject to laws similar to those which obtain in the case of the hydrocarbons. All experiments hitherto made warrant the conclusion that the behaviour of ethylic alcohol with the halogens (p. 462) is typical of all alcohols in which the OH groups are associated with carbon atoms forming part of an open chain, and derived from hydrocarbons in which the carbon atoms are either partially or entirely united in this manner; whilst the behaviour of phenol with the halogens, and indeed with reagents generally, appears to be more or less typical of all similarly constituted alcohols. The OH group in the alcohols has a very great "controlling" influence on substitution: this is shown especially by the behaviour of phenol, the tendency of this compound (p. 489) being always to form either ortho- or para-derivatives, whereas, it will be remembered, benzene furnishes chiefly meta-di-derivatives when submitted to the action of nitric and sulphuric acids; the influence of the OH in phenol is therefore similar to that of the halogens in the mono-haloid derivatives of benzene, and is different from that of the group NO_2 in nitrobenzene and of the group SO_3H in benzenesulphonic acid. The investigation of the extent to which substitution may be effected under ordinary conditions in the homologues of phenol indicates that the influence which the positive hydrocarbon radicles, or side chains, may exert in opposition to that of the negative OH group is dependent upon the relative "positions" of the latter and the former. Thus, in phenol itself, three atoms of hydrogen only are readily displaced under ordinary conditions: now thymol (p. 494) or methylpropylphenol, which, although a di-derivative of phenol, has only one of the side chains in a position in which substitution may be effected in phenol, behaves almost as a mono-derivative of the latter, yielding di-substitution derivatives under ordinary conditions; but metaxenol (p. 492) or orthoparadimethylphenol, in which both the side chains are in positions in which substitution may be effected in phenol, also readily furnishes di- and not mono-substitution derivatives when submitted to the action of bromine or of nitric acid:



Phenol.*



Thymol.



Metaxenol.

Apparently, therefore, the OH group in thymol is only influenced by one of the side chains—viz., that in the ortho-position, whilst the same group in metaxenol is influenced by both the side chains.

The OH groups in the dioxybenzenes appear to exert the same influence as in phenol: resorcinol, in which one of the hydrogen atoms is in the meta-position relatively to both groups, furnishing tri-substitution derivatives—tribromoresorcin, for example; whilst pyrocatechol, in which the hydrogen atoms are all either in the ortho-position or the para-position to one or other of the OH groups, is readily converted into tetrabromopyrocatechol.

The Carbohydrates.

(1553) This name is applied to a class of compounds allied to the hexhydric alcohols mannite and dulcite, consisting of carbon, oxygen, and hydrogen, the last two elements being always present in the same relative proportions as in water. Their composition is expressed by the formulæ $C_6H_{12}O_6$, $(C_6H_{12}O_6)_n$, $C_{12}H_{22}O_{11}$, and $(C_6H_{10}O_5)_n$, *n* in the last of these formulæ being always a whole number, which is probably never less than three; its value, however, has not yet been ascertained with certainty for any of the carbohydrates. They are physiologically of the greatest importance: only one class of compounds, in fact—the so-called albuminoids—being of equal importance, for they are the chief constituents of all plants, and are of constant occurrence in animal tissues.

The carbohydrates of the composition $C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$ are readily soluble in water, and more or less sweet to the taste:

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* The crosses indicate the "positions" in phenol in which alone substitution is effected under ordinary conditions.

ordinary sugar is a compound of the latter formula; those of the composition $(C_6H_{10}O_5)_n$ are mostly insoluble in water, as starch and cellulose, for example. The carbohydrates, like most of the polyhydric alcohols, readily undergo change when heated; but they seldom furnish well characterized products when submitted to the action of reagents. They are very readily oxidized, and many of the soluble carbohydrates have the property of reducing an alkaline solution of a cupric salt, cuprous oxide being precipitated; as different carbohydrates exhibit different reducing powers, and the amount of cuprous oxide precipitated is constant for a given variety, this property is of great service in differentiating and also in estimating the various carbohydrates. They are also characterized by the power which their solutions exhibit of causing the deviation of the plane of polarization of light, each carbohydrate differing in the extent to which it affects polarized light: a property which is equally of service as affording a means of distinguishing and of estimating soluble carbohydrates. We shall, therefore, before proceeding to the description of the individual carbohydrates, shortly describe the methods by which the *cupric oxide reducing power* and the *specific rotatory power* of soluble carbohydrates is determined.

(1554) *Determination of the Cupric Oxide Reducing Power of Soluble Carbohydrates.*—Dextrose being the substance of which the reducing power was first determined, it may be taken as the standard to which to refer all other carbohydrates, the cupric oxide reducing power being the amount of cupric oxide calculated as dextrose, $C_6H_{12}O_6$, which 100 parts reduce. Thus, the cupric oxide reducing power of dextrose being 100, that of maltose is 65, and that of milk sugar 70.

The cupric solution employed, which is usually termed Fehling's solution, is prepared by dissolving 35 grams of pure crystallized cupric sulphate in about 200 cc. of water, and in another vessel 173 grams of pure potassic sodic tartrate —so-called Rochelle salt—in 480 cc. of a solution of pure sodic hydrate of sp. gr. 1·14; the first solution is then added gradually to the second, and the deep blue-coloured clear fluid is diluted to 1000 cc. It must be kept in a cool, *dark* place, in well-closed bottles, filled to the top, as the action of light, or the absorption of carbonic anhydride would lead to the separation of cuprous oxide upon mere exposure to heat. Before using the solution, mix 10 cc. of it with 400 cc. of water, and boil the mixture for some minutes; if this produces the least change, and causes the separation of even the smallest quantity of cuprous oxide, the solution is unfit for use. Of this solution, 25—30 cc. are poured into a beaker of 130—140 cc. capacity, together with about 50 cc. of boiling well-boiled water; the beaker is then placed in a water bath, which is kept boiling, and at the end of five or six minutes, when the dilute copper solution has acquired as nearly as possible the temperature of the bath, a known quantity of the solution to be tested is added, and the heating continued for twelve or fourteen minutes. If the blue colour completely disappears in the first three or four minutes, it can be restored by adding quickly more copper solution, but if two or three additions be necessary to insure an excess, the experiment must be sacrificed, and a fresh one made with a smaller quantity of the carbohydrate solution. Satisfactory results cannot be obtained unless this precaution be adopted: the numbers generally falling too low with solutions of maltose or the glucoses, and too high when dextrin is also present, if the amount of cupric solution employed be not from the first in excess. After thirteen to fourteen minutes' heating, the precipitated cuprous oxide is rapidly filtered out, washed with boiling, well-boiled water, dried, and ignited in the usual way; strong ignition in an open porcelain crucible for five or six minutes completely converts the cuprous into cupric oxide, and treatment with nitric acid is unnecessary.

The time of heating above mentioned gives the true reduction for dextrose and maltose, and the quantity of cuprous oxide precipitated remains constant, even if the heating be continued for twenty minutes; but if the solution in addition contains dextrin, the reduction becomes greater, owing doubtless to the slow conversion of the dextrin into substances capable of acting upon the cupric solution (O'Sullivan, *Journ. Chem. Soc.*, 1876, ii. 130).

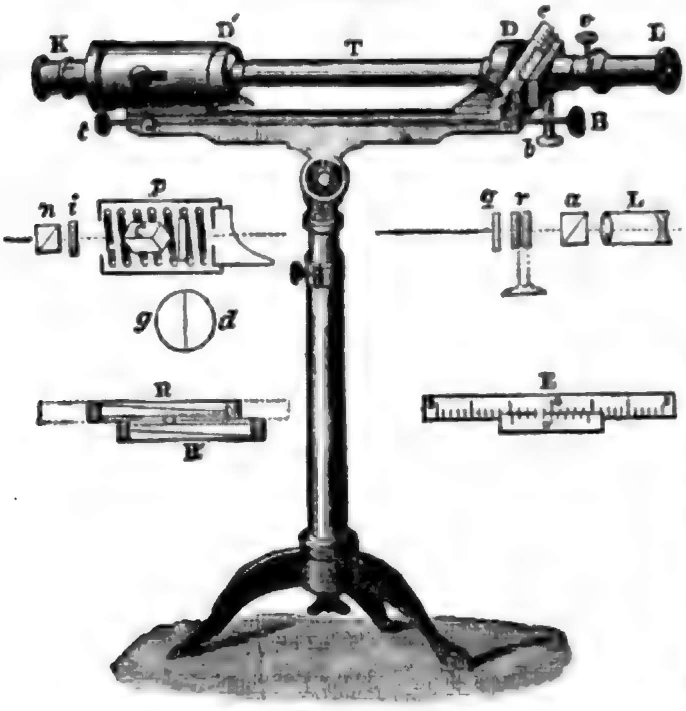
The cupric oxide reducing power is often determined volumetrically, the Fehling's solution being made with 34·639 grams crystallized cupric sulphate per litre, so that 10 cc. correspond to ·05 grams of dextrose: 10 cc. of the cupric solution and 40 cc. of water are heated in a water bath kept boiling, and the highly dilute solution of the carbohydrate is added in small quantities from a burette, until the bluish-green colour of the solution entirely disappears. Although concordant results may, with great care, be obtained by this process, the gravimetrical method is far more reliable, and involves very little more trouble in its execution.

(1555) *Determination of the Specific Rotatory Power of Optically Active Substances.*—The phenomena of polarization have been discussed in the first volume of this work (117—126). It has there been pointed out that if a polarized ray be transmitted through a plate of quartz cut at right angles to the optic axis of the crystal, the plane of polarization undergoes rotation in a degree proportional to the thickness of the plate, certain crystals of quartz producing right-handed, and certain others left-handed rotation. Many liquids, such as the terpenes, amylic alcohol, and solutions of cane sugar and other carbohydrates, of tartaric acid, and of a number of the alkaloids also exhibit this property, although to a much less marked extent than quartz. The manner of determining the degree of rotation produced by an optically active substance is as follows. Suppose a beam of monochromatic light, such as that given by a Bunsen flame in which a bead of sodic chloride or carbonate is heated, to pass through a pair of Nicol's prisms, one of which serves as polarizer, the other as analyser, and that the analyser is turned at right angles to the polarizer so that no light can pass through the latter: on interposing between them a plate of quartz, cut as above described, the field will become illuminated with yellow light, and it will be necessary to turn the analyser through a certain angle, either to the left or to the right, according as the quartz is cut from a right or left-handed crystal, to render the field dark again; or, what is the same thing, instead of rotating the analyser, the polarizer may be turned in the opposite direction. When ordinary white light is employed, the field never becomes dark, but assumes different tints as the analyser is rotated. The plate of quartz, in fact, causes the plane of vibration of the polarized ray to be deflected through an angle equal to that through which the analyser has been moved, but in the opposite direction: the quartz twisting the polarized ray in one direction, so to speak, and the analyser twisting it back again. It has been found, moreover, that the degree of rotation is directly proportional to the thickness of the plate; hence, if we know the amount of deviation produced by a given thickness of quartz, say a plate one millimetre thick, we can make it the standard of comparison for the deviation produced by other substances. If, instead of the sodium flame, any other kind of homogeneous light, red, green, or violet, be employed, similar results are obtained, but the angle of rotation varies, being least for red and greatest for violet light, as shown in the following table, which gives the deviation for a plate of quartz one millimetre in thickness, as determined by Biot:

	Deviation of Ray.		
Extreme red	17°	29′	47″
Red glass (oxide of copper)	18°	25′	00″
Limit of red and orange	20°	28′	47″
Limit of orange and yellow	22°	18′	49″
Mean yellow	24°	00′	00″
Limit of yellow and green	25°	40′	31″
„ of green and blue	30°	2′	45″
„ of blue and indigo	34°	34′	18″
„ of indigo and violet	37°	51′	58″
Extreme violet*	44°	4′	58″

All the instruments employed for determining the rotatory polarization of liquids consist essentially either of two Nicol's prisms, or of two double-refracting prisms, one of which serves as polarizer, and the other as analyser, between which a tube of known length—usually 200 mm.—is placed, containing the liquid under examination; but as it is difficult with a simple apparatus of this kind to determine when the light completely disappears, or when a particular tint appears, on rotating the analyser or polarizer, various devices are adopted to render the instrument more sensitive.

FIG. 392.



In Soleil's apparatus, one of the forms of which is represented in fig. 392, a biquartz or double plate, *gd*, one-half consisting of right-handed, and the other of left-handed quartz, 3·75 mm. thick, is placed behind the polarizer *c* at *p*. Quartz of this thickness produces at a certain position of the analyser, a peculiar pale rose-violet tint called the *sensitive* or *transition* tint from the rapidity with which it changes to rose or violet on moving the analyser; but the change of colour takes place in the opposite order in the two halves of the plate, so that although the whole field will

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* Broch gives the following number for the rotation produced by 1 mm. of quartz on light of the refrangibility of some of the chief lines in the solar spectrum:

B	C	D	E	F	G
15° 18′	17° 15′	21° 40′	27° 28′	32° 30′	42° 12′

De Luynes and Girard (*Compt. Rend.*, lxxx. 1354) have recently determined with great care the deviation produced by a plate 1 mm. in thickness, using a gas flame tinged by sodic chloride, the light from which is almost of the same refrangibility as the D line; they find 21° 48′, the possible error being at most four minutes.

appear uniformly coloured when the polarizer and the analyser are set with their principal sections parallel, the slightest rotation of the latter, or the introduction of an optically active substance between them, will cause one-half of the field to assume a redder, and the other a bluer shade than before. In this apparatus, however, in place of measuring the angle of rotation of the polarizer or analyser, the thickness of a plate of quartz required to neutralize the rotatory polarization of the liquid is estimated; but as the substance may be either dextrogyrate or lævogyrate, it is necessary to provide for the determination in both directions. This is done by inserting a plate of quartz of arbitrary thickness, *q*, cut from a right-handed crystal, between the analyser and the liquid to be examined, and immediately in front of this a compensator, *r*, a horizontal section of which is shown at RR′, consisting of two wedge-shaped pieces of quartz of contrary rotation to the plate *q*, but like it cut perpendicular to the axis of the crystal; these wedges can be moved one over the other by a toothed pinion fixed to the button *b*, acting on two racks adapted to the lower part of the mountings of the wedges, and are thus equivalent to a single plate whose thickness may be varied at pleasure. An ivory scale, *e*, represented separately at E, is attached to the mounting of one of the wedges, and a vernier to the other, the latter serving to measure the opposite displacements of the two wedges. When the zeros of the scale and vernier coincide, the two wedges are opposite to one another, and their thicknesses are together equal to that of the plate *q*, the rotatory power of which is therefore neutralized by them.

The liquid to be examined is contained in the tube T, placed between two perforated diaphragms DD′, one of which, D, is fixed, while the other, D′, can be removed at pleasure to a greater distance from D by a spring shown in section at *p*.

Before using the instrument for an observation, the tube T is filled with water, and the wedges are set so that the zeros of the scale and vernier coincide, and the analyser *a* is then turned by means of the endless screw, *v*, into such a position that on looking through the small telescope L, the two halves of the double plate *gd* appear uniformly coloured; or an uniformly coloured field is produced by adjusting the wedges, and the zeros of the scale and vernier are made to coincide by moving a screw connected with the former. If the tube T be now filled with the liquid to be examined, on placing it between the diaphragms DD′, the two halves, *g* and *d*, of the double plate will be found to exhibit very different colours; and to restore them to equality the compensator *r* must be so adjusted as to produce, together with the plate *q*, a rotation opposite to that of the liquid. The direction in which the vernier is moved along the scale indicates the direction of the rotation exercised by the liquid, and the displacement of the vernier gives the thickness of quartz required to neutralize this rotation when the thickness of quartz corresponding to one division of the scale is known. In the Soleil-Duboscq instrument, the scale is so graduated that 100 divisions correspond to 1 mm. of quartz, and the vernier is merely provided with a single mark, so that the thickness of the compensator required to neutralize the solution may be ascertained to the 100th of a millimetre.

Either ordinary daylight or the light from an argand lamp is employed. When either the light or the liquid in the tube is coloured, this colour, added to that produced by the polarization, modifies the sensitive tint and diminishes the accuracy of the observation. To neutralize this colour, in some instruments, a double-refracting prism, *n*, and a quartz plate, *i*, fixed in a socket which can be turned round in its own plane by means of a toothed wheel or pinion, *t*, and the button B are placed at K; but in others at L. The plate *i* yields a colour which may be varied by turning the prism *n*, so that a position of this prism may be found which gives a tint capable of sensibly neutralizing that of the liquid or light employed.

Soleil's apparatus is especially adapted to saccharine solutions, which, as Biot has shown, disperse light according to the same law as quartz, the angles of rotation for the different simple colours being approximately proportional to the squares of the indices of refraction, or inversely as the squares of the wave lengths; hence it is usually called a *saccharometer*. But it does not give good results with liquids such as a solution of tartaric acid, for example, whose rotatory power does not follow Biot's law; for determining the rotatory power of such liquids the observation must be made with monochromatic light, such as that of a Bunsen or spirit flame tinged yellow with sodic chloride or sodic carbonate.* The instruments most frequently employed for this purpose are Wild's polaristrobometer, and the Jellett-Cornu polarimeter, in both of which the angle is directly observed through which it is necessary to turn the polarizer or analyser so as to neutralize the polarization produced by a column of the liquid or solution under examination contained in a tube of known length.

In Wild's polaristrobometer a Savart double plate of quartz is placed behind the analyser, and between it and the tube containing the liquid; on rotating the polarizer, at certain positions the field appears perfectly bright, but at others is crossed by a number of dark striæ which are more or less marked according to the relative positions of the polarizer and analyser. The instrument is so adjusted that the zero point is indicated by the disappearance of these striæ. Supposing the field to be perfectly bright, on introducing the tube containing the rotating liquid, the striæ at once become visible, and in order to cause them to disappear the polarizer must be turned through a certain angle either to the right or to the left: this angle is directly observed by means of a divided circle attached to the polarizer. The polarimeter constructed by Hofmann of Paris is a similar instrument.

The Jellett-Cornu polarimeter consists simply of two Nicol's prisms, the analyser being one of ordinary construction, but the polarizer a double prism of peculiar construction. At a certain position of the analyser the two halves of the field appear equally illuminated, and this position, which may be determined with great precision, is the zero point of the instrument; the angular deviation is read off on a divided circle attached to the analyser (*Bull. Soc. Chim.*, 1870, xiv., 141).

Specific Rotatory Power.—The specific rotatory power of an optically active body is the angle through which the plane of polarization of a given ray is rotated by passing through a layer one decimetre in length of a liquid containing one gram of active substance in one cc.; therefore it is calculated by the formula:

$$[a] = \frac{a}{l \cdot \frac{c}{100}},$$

where a is the observed angle of deviation in degrees and decimals of a degree,
l, the length of the column of liquid in decimetres, and
c, the concentration, *i.e.*, the number of grams of active substance in 100 cc. of solution.

For example, a solution of cane sugar containing 10 grams in 100 cc. produces a deviation of 16°·32 in a tube 220 mm. long, the observation being made for the transition tint with a Soleil-Duboscq saccharometer; therefore:

$$[a]_j = \frac{16^\circ\cdot 32}{2\cdot 2 \times \cdot 10} = \frac{16^\circ\cdot 32}{\cdot 22} = 74^\circ\ 11'.$$

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* A bead of sodic chloride produces a much brighter light than one of the carbonate.

But if the concentration is measured by the number of grams p in 100 grams of solution, we have $c = d.p$, where d is the sp. gr. of the pure, active substance, or of its solution. For instance, a solution of dextrose of the specific gravity 1·0359 at 17°·5 (63°·5 F.) containing 9·3712 grams dextrose in 100 grams produces a deviation of 10°·25 in a tube 200 mm. long, the observation being made at 20° (68° F.) with the Wild polaristrobometer, using sodium light; hence:

$$[a]_D = \frac{10^\circ{\cdot}25}{2 \times 1{\cdot}0359 \times {\cdot}093712} = \frac{10^\circ{\cdot}25}{{\cdot}19416} = 52^\circ{\cdot}79.$$

When the observation is made for the transition tint, the specific rotatory power is indicated by the sign $[a]_j$, and when it is made with the sodium flame by the sign $[a]_D$; the signs a_j and a_D are respectively often employed to indicate the corresponding observed angular deviations.

When the determinations are made with any of the forms of the Soleil apparatus, the scale readings must be converted into degrees before the calculation can be made in the above manner. We have seen that in the case of the Soleil-Duboscq polarimeter the observation consists in determining the number of 100ths of a millimetre of quartz required to compensate the rotation produced by the liquid under examination, 100 divisions of the scale corresponding to the rotation produced by 1 mm. of quartz; 1 mm. of quartz, however, produces a rotation of 24° of the mean yellow; consequently the 100th of a millimetre of quartz corresponds to 0°·24, and it is merely necessary to multiply the scale reading by this number in order to obtain the number of degrees. For example, a solution containing 10 grams of cane sugar in 100 cc. requires for compensation 68 scale divisions or 68 hundredths of a millimetre of quartz, and hence produces a deviation of 68 × ·24 or 16·32 degrees. The scale of the Soleil-Ventzke saccharometer, an instrument much used in Germany, is somewhat less open, a solution of 16·19 grams cane sugar in 100 cc. causing a displacement of 100 divisions of the Soleil-Duboscq scale, but a solution of the sp. gr. 1·1 at 17°·5 (63°·5 F.) containing 26·048 grams of cane sugar in 100 cc. being required to produce an equal displacement of the Soleil-Ventzke scale (Landolt, *Zeits. anal. Chem.*, vii. 6). From this we may calculate that one division of the Soleil-Ventzke scale is equal to $\frac{26{\cdot}048}{16{\cdot}19}$ or 1·608 divisions of the Soleil-Duboscq scale, and *vice versâ*, that one division of the latter is equal to $\frac{16{\cdot}19}{26{\cdot}048}$ or ·621 of a division of the former; and, therefore, since one division of the Soleil-Duboscq scale is equal to 0°·24, a division of the Soleil-Ventzke (or Soleil-Ventzke-Scheibler) scale is equal to 0°·24 × 1·608 or 0°·3859.

The scale readings of the Soleil apparatus may be directly converted into degrees of rotation for sodium light in the following manner. 100 divisions of the scale of the Soleil-Duboscq saccharometer correspond to the deviation of 24° produced by a plate of quartz 1 mm. thick, but in any of the forms of polarimeter with which sodium light is employed a plate of this thickness causes a deviation of 21° 48′ = 21°·80 (footnote, p. 570); hence the rotation in sodium light corresponding to one division of the Soleil-Duboscq scale is $\frac{21{\cdot}80}{100} = 0^\circ{\cdot}218$. The rotation corresponding to one division of the Soleil-Ventzke scale is given by the proportion:

$${\cdot}24 : {\cdot}38 = {\cdot}218 : {\cdot}345.$$

If the specific rotatory power has been observed and calculated for the transition tint and it be desired to deduce from it the specific rotatory power for sodium light, or *vice versâ*, we may proceed as follows:

$$\cdot 24 : \cdot 218 = [\alpha]_j : [\alpha]_D$$
$$\cdot 218 : \cdot 24 = [\alpha]_D : [\alpha]_j,$$

Or more simply:

$$[\alpha]_j : 1{\cdot}10 = [\alpha]_D ; \quad [\alpha]_D \times 1{\cdot}10 = [\alpha]_j.$$

The specific rotatory power of a pure liquid substance is a constant number when its density and the angular deviation which it causes are always determined for the same temperature. If, however, solutions of such a substance with various inactive solvents be examined, values are obtained which differ more or less from that given by the pure substance, according to the nature of the inactive solvent and the proportion in which it is present, the specific rotatory power of some substances being increased, and that of others diminished on dilution. The same is true of solid substances; so that the value obtained for a given solution does not represent the specific rotatory power of the pure substance, but differs from it to an unknown extent dependent upon the influence which the inactive solvent exercises. The statement of the specific rotatory power of a substance in solution is therefore only of value when the composition of the solution is also cited. Moreover, the influence of a mixture of two solvents is often very different from that of either alone, and on this account it is necessary to use pure solvents, or if a mixture be employed, such as aqueous alcohol, accurately to ascertain its composition; the following table exhibits the alteration in the specific rotatory power of cinchonine according as it is dissolved in alcohol or chloroform, or a mixture of the two in various proportions (Oudemanns, *Ann. Chem. Pharm.*, clxvi. 70):

	Composition of the Solution.					$[\alpha]_D$
1	100·00	$CHCl_3$	+	0·00	C_2H_6O	+ 212°·0
2	99·66	,,	+	0·34	,,	+ 216°·3
3	98·74	,,	+	1·26	,,	+ 226°·4
4	94·48	,,	+	5·52	,,	+ 236°·6
5	86·95	,,	+	13·05	,,	+ 237°·0
6	82·26	,,	+	17·74	,,	+ 234°·7
7	65·00	,,	+	35·00	,,	+ 229°·5
8	44·29	,,	+	55·71	,,	+ 226°·6
9	27·54	,,	+	72·46	,,	+ 227°·6
10	17·02	,,	+	82·98	,,	+ 227°·8
11	0·00	,,	+	100·00	,,	+ 228°·0

The specific rotatory power of many substances is also influenced by temperature, being in some cases diminished, and in others increased. For example, at about 20° C. a rise of 1° C. reduces the angular deviation produced by a column 1 decimetre long of nicotine 0°·05, of orange peel oil 0°·19, and of an aqueous solution of invert sugar containing 17 grams in 100 cc. by 0°·11; on the other hand, the angular deviation is increased in the case of an aqueous solution of tartaric acid by a rise of temperature. It is therefore of importance always to take note of the temperature at which the angular deviation produced by a given liquid or solution is determined, and for accurate determinations it is desirable to surround the tube of the polarimeter with an outer casing, and to allow water of known temperature to circulate in the space between.

Inasmuch as the specific rotatory powers of various substances can only be properly compared together when the values which appertain to them in the pure state are known, and as the specific rotatory powers of solid bodies cannot as a rule be directly determined for the pure substances, but only for their solutions, it is of importance to be able to deduce the values for the former from observations made with solutions. Biot has shown that if the specific rotatory powers of a number of mixtures of an optically active liquid substance with an inactive chemically indifferent solvent are determined, and the variations represented graphically, the percentages by weight of the inactive solvent (q) being taken as abscissæ, and the corresponding values for $[\alpha]$ as ordinates, in some cases the increase or diminution in specific rotatory power is represented by a straight line, being proportional to the dilution, and may therefore be expressed by the linear equation:

$$\text{I. } [\alpha] = A + Bq,$$

A and B being constants deduced from the observations. In other cases a curve is obtained, which is usually a portion either of a parabola or of an hyperbola, and the relation of the specific rotatory power to q is represented by an expression of the form:

$$\text{II. } [\alpha] = A + Bq + Cq^2 + \ldots$$

or an equation having a greater number of constants.

With liquid bodies, commencing with the pure substance, the variation in specific rotatory power due to the influence of the solvent may be determined for all degrees of dilution, and the entire curve constructed from $q = 0$ almost to $q = 100$. In this case the specific rotatory power of the pure substance is put in place of A in the above formulæ, and the values calculated for B, or for B and C, then represent the increase or diminution of A due to 1 per cent. of the solvent. If $q = 0$ then $[\alpha] = A$: in other words, we have the specific rotatory power of the pure substance; but if $q = 100$, a number is obtained which expresses the specific rotatory power of the substance when diluted to an indefinite extent: that is to say, the maximum deviation of $[\alpha]$. But in the case of solids the value of A cannot be directly observed, and the extent to which the curve can be plotted is dependent upon the solubility of the substance. The constants of the formulæ I. and II. deduced from the observations are strictly available only for interpolation between the limits of concentration of the solutions actually employed, although if the variation in specific rotatory power is expressed by a straight line, that is to say, by the formula $[\alpha] = A + Bq$, the value of A may be determined by extrapolation. Obviously, however, if the variation be represented by a curve, the value deduced for A in the formula $[\alpha] = A + Bq + Cq^2$ will approximate less closely to the true value for the specific rotatory power of the pure substance the shorter the length of the curve which can be ascertained by experiment. The determination of the true specific rotatory power of a solid substance is therefore dependent on its solubility, and may at once be looked upon as hopeless if only dilute solutions can be prepared, and it is found that the increase or diminution in the value of $[\alpha]$ is not proportional to q. From this also it follows that the solvent employed should be that which is capable of dissolving the greatest quantity of the substance of which it is sought to determine the true specific rotatory power.

Landolt (*Deut. chem. Ges. Ber.*, ix. 901) concludes from his experiments that the degree of certainty with which the true specific rotatory power of a substance can be determined from that of its solutions is different for every substance, being dependent on the following circumstances: 1. On the degree of variation which the rotatory power of the substance undergoes under the influence of the solvent; 2. On the manner in which the variation is affected by an increase of the solvent, *i.e.*, whether the variation is expressed by a straight line or a line more or less curved; 3. On the concentration of the solution. In those cases in which the linear equation $[\alpha] = A + Bq$ is available for the calculation of A, the value deduced practically coincides with that observed for the pure substance, if the most concentrated solutions employed contain not less than about 50 per cent. of the active body: but if the variation be such that it is expressed by the parabolic equation $[\alpha] = A + Bq + Cq^2$, differences of more than 1° occur if solutions containing less than about 80 per cent. of active substance are employed.

In the following table given by Landolt, the specific rotatory power of a number of substances deduced directly from observations with the substances themselves, and indirectly from their solutions are given; the limiting values for $q = 0$ and $q = 100$ are stated, and it will be noticed how great in many instances is the variation of specific rotatory power due to the influence exercised by the inactive solvent:

	$[\alpha]_D$ For the Pure Substance. $q=0$	$[\alpha]_D$ For Maximum Dilution. $q=100$	Difference.
I. *Lævorotatory Turpentine Oil.*			
Directly observed	37°·01	—	—
Calculated from the alcoholic solution	36°·97	38°·79	1°·82
,, ,, solution in benzene...	36°·97	39°·79	2°·82
,, ,, ,, acetic acid	36°·89	40°·72	3°·83
II. *Dextrorotatory Turpentine Oil.*			
Directly observed	14°·15	—	—
Calculated from the alcoholic solution	14°·17	15°·35	1°·18
III. *Nicotine* (lævorotatory)			
Directly observed	161°·55	—	—
Calculated from the alcoholic solution	160°·83	138°·59	22°·24
,, ,, aqueous ,,	161°·24	74°·13	87°·16
IV. *Ethylic tartrate* (dextrorotatory).			
Directly observed	8°·31	—	—
Calculated from the alcoholic solution	8°·27	10°·19	1°·92
,, ,, solution in methylic alcohol	8°·42	11°·19	2°·77
,, ,, aqueous solution ...	8°·09	28°·12	20°·03

The substances included in this table are all liquids, but the same method is doubtless applicable to the determination of the specific rotatory powers of solids, as Biot has shown that the values deduced for cane sugar and tartaric acid from observations with their solutions agree with those obtained for the solids themselves.

The manner in which the quantity of an optically active substance present in a given solution may be estimated by the observation of its rotatory power will be described later on under dextrose, cane sugar, and starch.

We shall have occasion to refer to certain speculations as to the connexion between optical activity and constitution when discussing the constitution of the carbohydrates.

From the following description of the carbohydrates it will be evident that the correct determination of their specific rotatory power is of fundamental importance; and in concluding this account of the methods in use, we may direct attention to the necessity of extending the observations to solutions of various degrees of concentration, so as to enable the *true* specific rotatory power to be calculated. For most of the carbohydrates we are at present only acquainted with what may be termed the *apparent* specific rotatory power, *i.e.*, the specific rotatory power which they exhibit in solution, and with scarcely an exception the concentration of the solutions examined has varied within very narrow limits; in fact, the influence of all the various factors which affect the rotatory power, such as temperature, concentration, and nature of the solvent, has not been ascertained for a single optically active substance. As we have already observed, the composition of the solution from which the apparent specific rotatory power of the body under examination is deduced should always be stated, and also the temperature at which it is prepared, and at which the rotatory power is observed; moreover, in order to enable others to judge of the accuracy of the instrument employed, and of the method of observing, each operator should state the value he has found for *pure* cane sugar—a substance which may be procured without great difficulty, giving all the details of his method of operating.

The carbohydrates may provisionally be arranged in three groups, according to their composition. The first group includes all those represented by the formula $C_6H_{12}O_6$, and may be termed the glucose group. The second, or cane sugar group, includes those represented by the formula $C_{12}H_{22}O_{11}$. The third, or starch group, includes all carbohydrates represented by the formula $(C_6H_{10}O_5)_n$, in which *n* is always a whole number; but the members of this group form several sub-groups. We shall in the first place describe the chief properties of the individual carbohydrates, and afterwards discuss their genetic relations. It will often be more convenient, however, instead of describing all the members of one group before those of another, to consider a member of one group in connexion with a member of another to which it is intimately related.

I. *Carbohydrates of the Composition* $C_6H_{12}O_6$ *or Glucoses.*

(1556) SUCRODEXTROSE, DEXTROSE OR DEXTROGLUCOSE; *Glucose, Grape or Honey Sugar:* $C_6H_{12}O_6$.—This carbohydrate is widely distributed throughout the vegetable kingdom, being especially abundant in the juice of ripe sweet fruits—the name grape sugar being derived from its occurrence in considerable quantity in ripe grapes; it is also present in honey; but in most cases it is accompanied by sucrolævulose, and frequently also by cane sugar. It is obtained, together with an equal quantity of sucrolævulose, on heating a solution of cane sugar with dilute acids.

It is most conveniently prepared from crystallized honey, which is first spread out on a porous plate of plaster, or pressed between folds of bibulous paper, to free it as much as possible from the liquid portion. The nearly solid mass is then dissolved in alcohol, a small quantity of hydrochloric acid added, and the solution boiled for a short time in order to convert any cane sugar present into dextrose and lævulose; it is afterwards evaporated to a thin syrup in a flat dish at a gentle heat. The crystals which separate sooner or later from the syrup are washed with dilute alcohol, pressed, then triturated with strong alcohol, and afterwards washed on a filter with strong alcohol and recrystallized from water. If the crystals are coloured they may be again dissolved in a small quantity of water and treated with animal charcoal.

Sucrodextrose is soluble in a little more than its own weight of water at ordinary temperatures; if the solution be evaporated to a thin syrup it solidifies after a few days to a granular mass, but if evaporated to a thick syrup it does not solidify, owing to the absence of sufficient water, until it has absorbed moisture from the air. It generally separates from the aqueous solution in white opaque hemispherical or cauliflower-like masses of the composition $C_6H_{12}O_6 + OH_2$; when magnified, these aggregates are seen to consist of six-sided tables or prisms. At 17° (62°·6 F.) it requires about 50 pts. of alcohol of sp. gr. ·83 to dissolve it, but only about 5 pts. of the boiling alcohol; it crystallizes from anhydrous alcohol in small well-defined prisms without water of crystallization. It is much less sweet to the taste than cane sugar. The hydrated crystals melt at 86° (186°·8 F.), and the anhydrous compound at 146° (294°·8 F.) (Schmidt, *Ann. Chem. Pharm.*, cxix. 92); at 82° (179°·6 F.) and 144° (291°·2 F.) (Hesse, *ibid.*, clxxvi. 103). On heating to about 170° (338° F.) it loses the elements of a molecule of water, and is converted into glucosan, $C_6H_{10}O_5$; if the heating be continued, caramel-like substances are produced. The hydrated crystals of dextrose may be rendered almost completely anhydrous by heating to about 70° (158° F.), the last traces of water being given off at a temperature below 100° (212° F.) (Hesse). The anhydrous crystals deposited from alcohol are not hygroscopic, but anhydrous dextrose which has undergone fusion rapidly absorbs water in moist air.

According to various observers (Dubrunfaut, Schmidt, Hesse), a freshly prepared solution of either the anhydrous or hydrated crystals, or of sucrodextrose which has been rendered anhydrous without fusion, has an apparent specific rotatory power calculated for the anhydrous substance of $[\alpha]_j = +101° - 106°$; the optical activity gradually diminishes, however, to half this, and then remains constant. This diminution of rotatory power takes place slowly at 0° (32° F.), but is complete in 24 hours at the common temperature, or in a few minutes at 100° (212° F.); moreover, a freshly prepared solution of dextrose which has undergone fusion at once exhibits the lower rotatory power.

The constant apparent specific rotatory power of sucrodextrose at the ordinary temperature observed for solutions containing 10 per cent. or thereabouts, and calculated for the anhydrous substance, is somewhat variously stated—viz., $[\alpha]_j = +53^{\circ}{\cdot}2$ (Dubrunfaut), 56° (Berthelot), 57° (Schmidt), $57^{\circ}{\cdot}4$ (Béchamp), $57^{\circ}{\cdot}6$ (O'Sullivan); and $[\alpha]_D = 50^{\circ}{\cdot}9$ (Hesse), 53° (Tollens): the higher values are doubtless the more correct.*

Dextrose furnishes a number of unstable metallic derivatives, most of which are soluble in water; their composition has only been imperfectly determined, but excepting the lead derivatives they appear to be formed by the displacement of at most two atoms of hydrogen. Thus, on mixing alcoholic solutions of dextrose and potassic hydrate, a white gelatinous precipitate of a potassium derivative is obtained, which, however, soon becomes brown. An aqueous solution of dextrose dissolves considerable quantities of the hydrates of barium, strontium, or calcium, forming yellow solutions precipitable by alcohol, which, even if protected from the air, become darker and are decomposed when kept or heated. A solution of dextrose is not precipitated by either normal or basic lead acetate, but an ammoniacal solution of the normal acetate produces a white precipitate. In the presence of alkali a solution of dextrose dissolves a large quantity of cupric hydrate, forming a deep blue coloured liquid, from which cuprous oxide separates after some time on standing at the ordinary temperature, and quickly on heating; according to Claus (*Journ. pr. Chem.* [2], iv. 96), one molecule of dextrose dissolves three molecules of cupric hydrate, the solution of each molecule of the latter, however, being dependent on the presence of a certain fixed quantity of alkali.

On allowing a concentrated solution of sucrodextrose and sodic chloride in the proportion of two mols. of the former to rather more than one mol. of the latter to evaporate over sulphuric acid, the compound $2C_6H_{12}O_6.NaCl + OH_2$ separates in large colourless lustrous crystals. An analogous compound with sodic iodide, $2C_6H_{12}O_6.NaI$, may be still more readily prepared (C. H. Gill, *private communication*).

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* The influence of temperature and concentration on the apparent specific rotatory power of pure sucrodextrose from cane sugar or honey requires investigation: apparently temperature has but little influence, but according to Hesse's observations (*loc. cit.*), the rotatory power diminishes slightly with the concentration for solutions containing from 1 to 12 grams per 100 cc., whereas from Tollens' observations (*Deut. chem. Ges. Ber.*, ix. 1531) it appears that commencing with solutions containing 10—14 per cent. the rotatory power increases considerably with increase of concentration (see Starch); it is not improbable, however, that Hesse's higher values are due to slight errors of observation, which tend the more to disturb the result the weaker the solution for which the observation is made, an error of $5'$ making a difference of no less than 4° in the specific rotatory power in the case of a solution containing only 1 gram in 100 cc.

On heating dehydrated crystallized dextrose with about 2½ times its weight of acetic anhydride in an open vessel a violent reaction takes place, and a mixture of a di- and triacetate: $C_6H_{10}(C_2H_3O_2)_2O_4$ and $C_6H_9(C_2H_3O_2)_3O_3$, is produced, which may be separated by boiling benzene, as the latter only is soluble in this liquid; they are amorphous, bitter tasting substances, soluble in water. By heating the triacetate with a large excess of acetic anhydride for six hours at 160° (320° F.), it is converted into the octacetate of a compound formed by the withdrawal of the elements of a molecule of water from two molecules of dextrose: $C_{12}H_{14}(C_2H_3O_2)_8O_3$; this is an amorphous tasteless substance, insoluble in water. These acetyl derivatives of glucose are all dextrorotatory (Schützenberger, *Ann. Chim. Phys.* [4], xxi. 235).

By the action of an excess of acetic chloride at ordinary temperatures, dextrose is readily converted into the chloracetin $C_6H_7Cl(C_2H_3O_2)_4O$ (acetochlorhydrose), which on treatment with cold highly concentrated nitric acid yields the nitracetin $C_6H_7(NO_3)(C_2H_3O_2)_4O$. The former compound crystallizes with difficulty; the latter crystallizes readily in oblique prisms or large rhombic plates, insoluble in water, but soluble in alcohol, and melts at 145° (293° F.) without decomposition. Both are more powerful dextrorotatory substances than dextrose (Colley, *Compt. Rend.*, lxx. 401; lxxvi. 436; *Ann. Chim. Phys.* [4], xxi. 366).

If perfectly anhydrous, and it be added gradually, dextrose dissolves in concentrated sulphuric acid without causing the discoloration of the liquid, thus differing from cane sugar which, unless the greatest care be taken, is at once carbonized; an acid ethereal salt, probably analogous to the acid sulphate of glycerin (p. 540) is formed, but on account of the readiness with which this salt is reconverted into its generators by water, its composition has not yet been satisfactorily ascertained. The exact composition of the nitrate formed on treating dextrose with highly concentrated nitric acid is also unknown.

As already stated (p. 556), sucrodextrose is converted into mannitol by the action of nascent hydrogen.

Characteristic products have not as yet been obtained from it by the action of the halogens, of the haloid acids, or of the haloid phosphorus compounds, chiefly because of the difficulty of avoiding its complete decomposition by these reagents (comp. Colley, *loc. cit.*).

It is very readily decomposed by alkalies, a solution to which an alkali has been added rapidly becoming yellow and then brown when heated, and if the heating be continued humus-like substances separate; a similar change slowly ensues at ordinary temperatures. According to Peligot, the product of the moderated action of alkalies is an amorphous very soluble substance, precipitable by basic plumbic acetate, which he terms glucic acid; he assigns to it the formula $C_{12}H_{18}O_9$, but this cannot be regarded as established, and more recent researches have failed to throw light on the nature of the reaction. By heating dextrose with sodic hydrate solution in the proportion of 500 grams of the former to 500 cc. of a solution of the latter of the sp. gr. 1·34 diluted with an equal volume of water, Hoppe-Seyler (*Deut. chem. Ges. Ber.*, iv. 346) has obtained ordinary fermentation lactic acid, together with formic acid, which is the only volatile acid produced, small quantities of pyrocatechol, and uncrystallizable substances of unknown composition. The reaction commences at about 96° (204°·8 F.), and is extremely violent, the temperature of the liquid rising to about 116° (240°·8 F.). The lactic acid produced amounts to 10—20 per cent. of the air-dry sugar.

Dextrose is also acted upon with extreme facility by oxidizing agents. It has already been pointed out that it easily reduces an alkaline solution of cupric sulphate; numerous experiments have shown that exactly five molecules of the cupric salt are reduced, and two and a half molecules of cuprous oxide precipitated for each molecule of dextrose oxidized,* and it is on this fact that the method for the estimation of dextrose described on pp. 568—569 is based. Dextrose is also oxidized by an alkaline solution of potassic ferricyanide; it precipitates silver from a solution of argentic nitrate on boiling; it reduces ferric to ferrous salts, and on heating it with a solution of sodic carbonate and basic bismuthic nitrate, a black-brown liquid and greyish-brown precipitate are obtained. On boiling it with an alkaline solution of mercuric cyanide, metallic mercury is precipitated; Knap has based on this reaction a method for the determination of dextrose (*Ann. Chem. Pharm.*, cliv. 252), which, however, according to Sachsse, is not reliable (see Cane Sugar, Estimation of).

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* Although the amount of cupric salt reduced by a given quantity of dextrose is constant, the nature of the reaction has not been ascertained, but it is apparently extremely complex. Thus, from a number of experiments on the action of cupric hydrate in presence of potassic hydrate, Claus (*Ann. Chem. Pharm.*, cxlvii. 114; *Journ. pr. Chem.* [2], iv. 63) considers that the products are of three kinds—viz.: 1. Acetic and formic acids. 2. A mixture of non-volatile acids containing tartronic acid, which can be separated in the crystalline state, and which furnishes crystalline salts; an acid which is readily decomposed on heating its aqueous or ammoniacal solution, with separation of humus-like substances; and at least one other acid, which is not only itself uncrystallizable, but also furnishes uncrystallizable salts. 3. A gum-like substance.

When dextrose is heated with bromine and water, it yields hydrobromic acid, a dark brown liquid, and humus-like products; but on passing chlorine into a cold dilute aqueous solution of dextrose as long as absorption takes place, then expelling the dissolved chlorine by a current of carbonic anhydride, treating the warmed liquid with argentic hydrate until neutral, and precipitating the dissolved silver by sulphuretted hydrogen, a solution of gluconic acid is obtained (Hlasiwetz and Habermann, *ibid.*, clv. 123). Gluconic acid is a syrup, but its baric, calcic, and ethylic salts crystallize well; it has the composition $C_6H_{12}O_7$, and is perhaps a monobasic acid of the formula $CH_2(OH)(CH.OH)_4.COOH$. By boiling with dilute nitric acid, dextrose is oxidized to saccharic acid, $COOH.(CH.OH)_4.COOH$, and oxalic acid. On distillation with oxidizing agents such as manganic peroxide and sulphuric acid, it yields formic acid.

A dilute aqueous solution of dextrose readily undergoes alcoholic fermentation when mixed with beer yeast, 100 pts. dextrose yielding 48—49 pts. alcohol.

(1557) *Dextroglucoses from various sources, which are perhaps identical with Sucrodextrose.*—A number of glucosides (q.v.) furnish bodies of the composition $C_6H_{12}O_6$ when decomposed by heating with dilute acids, but scarcely any of the glucoses thus obtained have been sufficiently examined to enable us to say that they are, or are not, identical with sucrodextrose. According to Schmidt (*ibid.*, cxix. 92), the glucoses from salicin and amygdalin have the same rotatory power as sucrodextrose prepared from honey; Hesse (*ibid.*, clxxvi. 112), however, states that he found them possessed of a slightly higher rotatory power, and that glucose from salicin parts with its water of crystallization much more readily than sucrodextrose, but it would appear from his statements that on dehydrating salicin-dextrose crystallized from water it is converted into sucrodextrose. Whether the differences observed by Hesse are really inherent, however, or due to impurity or imperfect observation, can only be decided by a more careful examination. According to the same observer, the dextrose from phloridzin is essentially different from sucrodextrose: the hydrated crystals melt at 74° (165°·2 F.); they lose only 6·7 per cent. of their water of crystallization when heated to 60°—70° (140°—158° F.); and require the temperature to be raised to 105° (221° F.) in order to expel the last traces of water. It also differs from sucrodextrose in optical activity, its apparent specific rotatory power calculated for the anhydrous substance in a solution containing 3 per cent. of the hydrate $C_6H_{12}O_6 + OH_2$ being for the freshly-prepared solution $[\alpha]_D = 89°$, and after standing $[\alpha]_D = 44°$.

According to Will and Körner (*Ann. Chem. Pharm.*, cxxv. 275), the glucose obtained from myronic acid is identical with sucrodextrose. It crystallizes from water in cauliflower-like masses of the composition $C_6H_{12}O_6 + OH_2$, which melt at 86° (186°·8 F.), and from absolute alcohol in anhydrous nodules consisting of fine needles, which melt at 144°—146° (291°·2—294°·8 F.). It is dextrorotatory—to what extent is not stated—and has the same cupric oxide reducing power as sucrodextrose.

Zwenger and Hind (*ibid.*, cxviii. 149) state that the glucose from solanin has all the properties of sucrodextrose, but they only mention that it crystallizes in colourless, well-formed, apparently rhombic prisms.

According to Brücke and Bence Jones, dextroglucose occurs in small quantity in normal urine, and it is present in considerable quantity, even to the extent of eight or ten per cent., in diabetic urine. It is generally stated that dextrose from diabetic urine is identical with sucrodextrose, but apparently this is by no means established. Thus, Hoppe-Seyler, in 1865, using diabetic sugar ten to twelve times recrystallized from alcohol, found the apparent specific rotatory power for a solution containing 36 grams in 100 cc. to be $[\alpha]_D = 53^{\circ}{\cdot}45$; a later determination with a Wild's polaristrobometer gave $[\alpha]_D = 52^{\circ}{\cdot}1$, the previous determination having been made by Broch's method for the Fraunhofer line D. Recently (*Zeits. anal. Chem.* 1875, xiv. 303) he has obtained the mean value $[\alpha]_D = 56^{\circ}{\cdot}4$ for solutions containing from 4·5 to 26 per cent. by weight of the anhydrous dextrose, which had been carefully purified by often-repeated crystallization from alcohol; this value is considerably higher than that given by sucrodextrose, and would appear to indicate that dextrose from diabetic urine is not identical with sucrodextrose. Pasteur (*Ann. Chim. Phys.* [3], xxxi. 92) found the apparent specific rotatory power of the sodium chloride compound $2C_6H_{12}O_6.NaCl + H_2O$ prepared from diabetic sugar to be $[\alpha]_j = 47^{\circ}{\cdot}14$, and on the supposition that the dextrose in this compound retains its proper optical activity unmodified, we may calculate its apparent specific rotatory power by the proportion

$$436{\cdot}4 : 360 = 47^{\circ}{\cdot}14 : 57^{\circ}{\cdot}1\,;$$

and thus obtain a value agreeing nearly with that directly observed for sucrodextrose.*

The dextroglucoses from cellulose, glycogen, and starch will be described later on, when these compounds are considered.

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* The rotatory power of the sodium chloride compound prepared from sucrodextrose has apparently not been determined. According to Stædeler, the compounds $C_6H_{12}O_6.NaCl$ and $2C_6H_{12}O_6.2NaCl + H_2O$ sometimes separate from diabetic urine containing sodic chloride.

The determination of the nature of the dextrose in diabetic urine is of importance apart from its scientific value, as the optical method is usually employed in estimating the amount of sugar in urine. The deviation produced by the urine in a tube of known length having been ascertained, the number of grams of sugar (x) contained in 100 cc. is calculated by the formula

$$x = \frac{100 \cdot \alpha_j}{[\alpha]_j} \quad \text{or} \quad \frac{100 \cdot \alpha_D}{[\alpha]_D},$$

according as the observation is made for the transition tint or with sodium light, α_j or α_D being the observed angular deviation for a column one decimetre long, and $[\alpha]_j$ or $[\alpha]_D$ the apparent specific rotatory power of the sugar present; *i.e.*, if diabetic sugar is identical with sucrodextrose $[\alpha]_j = 58^{\circ}$, and $[\alpha]_D = 53^{\circ}$. This is on the assumption that the apparent specific rotatory power is independent of concentration, which is probably not the case; but the variation for solutions containing from 5 to 20 per cent. is apparently so slight that it does not appreciably affect the result.

(1558) SUCROLÆVULOSE OR LÆVULOSE; *Lævoglucose:* $C_6H_{12}O_6$. —This carbohydrate occurs mixed with sucrodextrose in honey; in many fruits and other sacchariferous vegetable organs (comp. Buignet, *Ann. Chim. Phys.* [3], lxi. 233; J. Boussingault, *Compt. Rend.*, lxxxiii. 978); and is produced, together with an equal quantity of sucrodextrose, on heating a solution of cane sugar with dilute acids, the mixture of the two carbohydrates in equal proportions constituting so-called invert sugar, from which it was first separated in a pure state by Dubrunfaut in 1847. The lævoglucose obtained on heating inulin with dilute acids, according to Dubrunfaut, is identical with sucrolævulose, but this statement requires confirmation. The isolated occurrence of sucrolævulose has not yet been demonstrated; it is remarkable also that none of the glucosides hitherto examined furnish lævorotatory glucose.

It may be prepared by Dubrunfaut's method (*Compt. Rend.*, lxix. 1366), which consists in adding six parts finely powdered calcic hydrate to a *cold* solution of ten parts invert sugar in 100 parts water; as the lime is added, the mixture is well shaken, the flask being occasionally plunged into ice-cold water in order to prevent rise of temperature. A milky liquid is thus obtained, which, however, after a time becomes pasty, owing to the separation of a difficultly soluble calcium derivative of lævoglucose. It is then thrown on a linen filter, and the solution containing the dextrose having drained away, the residue is washed, then strongly pressed, and afterwards suspended in water and decomposed either with oxalic or carbonic acid. On concentrating the filtered liquid, the lævulose is obtained as a colourless, uncrystallizable syrup, or as an amorphous gum-like mass, much sweeter than sucrodextrose, and more soluble in alcohol.

The properties of pure sucrolævulose have been little studied. Its apparent specific rotatory power in aqueous solution diminishes or increases in proportion as the temperature rises or falls: thus at 14° (57°·2 F.) $[\alpha]_j = -106°$; at 52° (125°·6 F.) it is $-79°·5$; and at 90° (194° F.) it is $-53°$. Like sucrodextrose, it furnishes a soluble calcium derivative, in addition to the sparingly soluble one above mentioned; the latter crystallizes in microscopic needles, and is formed by the displacement of three atoms of hydrogen by calcium (Dubrunfaut). It does not appear to combine with sodic chloride (C. H. Gill); neither does it retain water, like dextrose, as the residue obtained on evaporating its aqueous solution in vacuo over sulphuric acid has the composition $C_6H_{12}O_6$ (Dubrunfaut, *ibid.*, xlii. 901). When rapidly heated to about 170° (338° F.) it is converted into lævulosan, $C_6H_{10}O_5$. Its conversion into mannitol has already been mentioned (p. 556).* It is more readily decomposed by acids (see Cane Sugar), but less readily by alkalies than dextrose; and in contact with beer yeast it ferments less readily than the latter. It has the same cupric oxide reducing power as dextrose, but it does not exhibit the same behaviour as the latter with all oxidizing agents, since, according to Sachsse (see Cane Sugar, Estimation of), the reducing power of invert sugar is less when tested by an alkaline solution of mercuric iodide than when tested by Fehling's solution. Moreover, by passing chlorine into an aqueous solution of lævulose, and afterwards saturating the liquid with argentic hydrate, &c., Hlasiwetz and Habermann (*Ann. Chem. Pharm.*, clv. 130) obtained glycolic acid, $CH_2(OH).COOH$, dextrose, as we have learnt, being converted by this treatment into dextronic acid, $C_6H_{12}O_7$: and they assume that three molecules of this acid are formed from a single molecule of lævulose. Krusemann, however, who has prepared glycolic acid in a similar manner from inulin-lævulose, states that the amount obtained is exceedingly small, and not sufficient to warrant the assumption that a single molecule furnishes three molecules of glycolic acid (*Deut. chem. Ges. Ber.*, ix. 1468). It is said to furnish saccharic acid on oxidation with nitric acid.

(1559) LACTOSE; *Galactose:* $C_6H_{12}O_6$.—The discovery that milk sugar, when boiled with dilute sulphuric acid, furnishes a glucose isomeric with sucrodextrose is generally attributed to Pasteur, it having escaped the notice of most chemists that A. Bouchardat had previously (in 1851) isolated a body apparently different from sucrodextrose. The glucose obtained by Bouchardat, however, had the apparent specific rotatory power $[\alpha]_r = 45^{\circ}{\cdot}9$ (or $[\alpha]_j = 59^{\circ}{\cdot}8$),† and gave only traces of mucic acid on oxidation;

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* Both dextrose and lævulose, when submitted to the action of sodium amalgam in aqueous solution, furnish a small quantity of a mixture of alcohols of the ethylic series, consisting of ethylic, isopropylic, and hexylic alcohols, the last of which is perhaps identical with the secondary hexylic alcohol from mannitol (Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 87; Krusemann, *Deut. chem. Ges. Ber.*, ix. 1465). Ordinary lactic acid is also produced in considerable quantity; Bouchardat attributes its formation to the action of the sodic hydrate, and not to that of the nascent hydrogen, but it is by no means improbable that it is, in part at least, a direct product of the action of the latter.

† It was customary when Biot's original form of apparatus was employed to interpose a plate of glass coloured red with oxide of copper between the polarizer and the tube containing the liquid, and the symbol $[\alpha]_r$ is that used to indicate the specific rotatory power observed in this manner for red light. Now,

whereas that obtained by Pasteur (*Compt. Rend.*, xlii. 347, 1856), gave about twice as much mucic acid on oxidation as milk sugar did, its apparent specific rotatory power in a 2 per cent. solution immediately after the preparation of the solution being $[a]_j = 139°·6$, and after twenty-four hours $83°·2$. Lactose, according to Pasteur, crystallizes more readily than sucrodextrose, but generally in nodules like the latter; sometimes, however, it forms microscopic rectangular prisms, acuminated at the edges, but more often six-sided, round-edged laminæ, having a pea-shaped protuberance in the middle. It has the same cupric oxide reducing power as sucrodextrose. He was unable to obtain from it a compound with sodic chloride.

Obviously the glucoses examined by Bouchardat and Pasteur differ considerably in properties; and hence it would appear probable that two dextrorotatory glucoses are simultaneously produced on inversion of milk sugar. Fudakowski has shown that this is really the case, and that they may be separated in the following manner (*Medicinisch-chemische Unt. a.d. Lab. für angewandte Chemie zu Tübingen*, 1866, i. 164; *Deut. chem. Ges. Ber.*, viii. 599; ix. 42). Pure milk sugar is boiled with a mixture of 2 vols. water and 1 vol. dilute (1 : 5) sulphuric acid until the liquid acquires a pale brown colour, water being added to replace that lost by evaporation; this requires about an hour. When cold, the solution is neutralized with calcic carbonate, a slight excess of baryta water is then added, and it is saturated with carbonic acid. The filtered liquid is now evaporated to a thin syrup, and to this alcohol is added, which causes the separation of *a-lactose*, whilst *β-lactose* crystallizes after some time from the mother liquor; the two bodies are purified by recrystallization, with the aid of animal charcoal, from 95—98 per cent. alcohol, in which the latter is considerably the more soluble. a-Lactose crystallizes in small rectangular prisms with two end faces; β-lactose forms granules and occasionally six-sided tables, such as

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according to Biot, a plate of quartz one mm. in thickness produces a deviation of 18° 25′ or 18°·41 of the light passing through red glass, and a deviation of 24° of mean yellow light (p. 573); hence

$$[a]_r : [a]_j = 18·41 : 24,$$

and therefore

$$[a]_j = \frac{[a]_r \cdot 18·41}{24}$$

Red glass, however, differs in quality, and on this account the value of $[a]_j$, calculated from that of $[a]_r$, can be regarded as approximate only, unless the quality of the glass employed is known.

are described by Pasteur, containing, even when crystallized from 98 per cent. alcohol, a molecule of water, the greater part of which, however, is expelled at 60° (140° F.). The latter appears to have a sweeter taste, and to be more soluble and more easily fermentable than the former. Their freshly prepared solutions in cold water, like that of sucrodextrose, have a much higher rotatory power than after long-standing or warming; the values obtained for the two sugars by Broch's* method, after heating the solutions, were as follows:

α-Lactose† (in a solution containing 13 per cent.) $[\alpha]_D = 92^\circ{\cdot}83$
β-Lactose („ „ 18 „) $[\alpha]_D = 62^\circ{\cdot}83$.

By oxidizing α-lactose with nitric acid, Fudakowski obtained 32 per cent. of its weight of pure mucic acid dried at 100° (212° F.); β-lactose on treatment of its aqueous solution with chlorine and afterwards with argentic hydrate, &c., was converted into an acid of the same composition as gluconic acid (p. 582), but which furnished a crystalline baric salt containing only a single molecule of water, whereas that obtained by Hlasiwetz and Habermann from dextrose contained three molecules of water.

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* The determination of the specific rotatory power by Broch's method is effected by a combination of the polarimeter with the spectroscope, and is the most accurate of all methods. By means of a heliostat, sunlight is reflected into a dark room through a narrow slit, and the rays are rendered parallel by an achromatic lens, fixed in such a position that the slit is in its focus; the polarimeter, consisting merely of a polarizer and analyser, is placed behind the lens, and the beam which issues from the analyser is then allowed to fall on a prism, in front of which is fixed a telescope for the observation of the spectrum. The tube containing the liquid under examination is placed in the usual manner between the two Nicol's prisms. The white light which falls on the Nicol placed nearest to the slit becomes polarized in a particular plane, but in its passage through the polarizing liquid the plane of polarization is deflected to an extent which varies for each component of the white light; the colour whose plane of polarization is perpendicular to the plane of vibration of the analysing Nicol, therefore, cannot pass through the latter, so that the spectrum observed through the telescope exhibits, in addition to the ordinary Fraunhofer lines, a black band which shifts from one end of the spectrum to the other as the analyser is rotated. The observation consists in adjusting the vertical spider line in the eye-piece of the telescope so that it coincides with a particular Fraunhofer line, the D line for example, and the analyser is then rotated until the centre of the black band and the spider line are coincident; the angle through which the analyser has been moved from its original position before the polarizing liquid was introduced is then read off on the divided circle attached to it, and the angular deviation of light of the refrangibility of the particular line observed is thus determined.

† In distinguishing isomeric carbohydrates by the letters α, β, &c., it appears desirable to attribute a definite signification to these letters, and to assign α to the body which has the higher, and β to that which has the lower specific rotatory power.

A solution of milk sugar inverted by boiling with sulphuric acid yields a mixture of dulcitol and mannitol when submitted to the action of sodium amalgam, and as the glucose of high rotatory power from milk sugar yields only dulcitol when similarly treated, we may conclude that α-lactose is converted into dulcitol, and β-lactose into mannitol, by the action of nascent hydrogen (G. Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 79).

There can be no doubt from Pasteur's and Fudakowski's observations that α-lactose is a body altogether different from sucrodextrose; and if it be supposed that the β-lactose obtained by the latter chemist was free from α-lactose, it would follow that it is also an isomeride of sucrodextrose as it has a considerably higher rotatory power. β-lactose, however, in many respects closely resembles sucrodextrose, which, according to Pasteur, also crystallizes in six-sided laminæ, although these do not exhibit the peculiar protuberances above mentioned. Moreover, Dubrunfaut has stated that when a solution of milk sugar undergoes inversion the rotatory power increases until finally it becomes $\frac{13}{10}$ths of its original value; the apparent specific rotatory power of milk sugar being $[\alpha]_j = 59^\circ\cdot 3$, the rotatory power of the invert sugar from it would therefore be $59\cdot 3 \times \frac{13}{10} = 77^\circ\cdot 1$. Now, if the theoretical rotatory power be calculated from Fudakowski's values above given, we obtain a much higher number than this; thus:

$$\frac{92^\circ\cdot 8 + 62^\circ\cdot 8}{2} = 77^\circ\cdot 8, \text{ and hence } [\alpha]_j = 77^\circ\cdot 8 \times 1\cdot 1 = 85^\circ\cdot 5.$$

But if we assume that invert milk sugar is a mixture of α-lactose and sucrodextrose, and that Fudakowski's value for the former is correct,* we have:

$$\frac{92^\circ\cdot 8 + 53^\circ\cdot 1}{2} = 72^\circ\cdot 95, \text{ and hence } [\alpha]_j = 72^\circ\cdot 95 \times 1\cdot 1 = 80^\circ\cdot 24,$$

which is a much closer approximation to Dubrunfaut's value. It is to be observed also that the rotatory power of Bouchardat's product (p. 585), which gave only traces of mucic acid on oxidation, and which, therefore, we may suppose was not much contaminated by α-lactose, is only slightly higher than that of sucrodextrose. Hence it appears not improbable that milk sugar on inversion is converted into sucrodextrose and an isomeric glucose of much higher rotatory power. The most suitable name for the latter is lactose, being that originally assigned by Pasteur to the product which he isolated from inverted milk sugar, although from Pasteur's description there can be little doubt that his experiments were made with a mixture only chiefly consisting of lactose.

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* G. Bouchardat (*loc. cit.*, p. 83, 1872) states that, by recrystalling from alcohol the crystals which first separate from the concentrated solution of inverted milk sugar, he obtained a product having the apparent rotatory power (in a 7·5 per cent. solution) $[\alpha]_j = 82^\circ\cdot 9$, which nearly agrees with that observed by Pasteur. But the sign $[\alpha]_j$ is incorrectly used by Bouchardat, who employed a polarimeter illuminated by sodium light; the value $[\alpha]_D = 82^\circ\cdot 9$ or $[\alpha]_j = 91^\circ\cdot 2$ is considerably higher than Pasteur's, although lower to about an equal extent than that observed by Fudakowski.

(1560) **Arabinose**; *Pectinose:* $C_6H_{12}O_6$.—This glucose is obtained by heating "arabin" from the sugar-beet, or gum arabic, with dilute sulphuric acid, and was first described by Scheibler in 1868 (*Deut. chem. Ges. Ber.*, i. 58, 108; vi. 612); its preparation will be described later on. It crystallizes in very brittle, colourless, glistening, anhydrous, rhombic prisms with dihedral summits, which are mostly concentrically arranged; the crystals are sweet to the taste, although less sweet than cane sugar. When carefully heated, it melts at about 160° (320° F.), but decomposes at higher temperatures. It is extremely soluble in hot water, but the excess crystallizes out at once on cooling. It is charred by concentrated sulphuric acid; on oxidation with nitric acid it is converted into oxalic acid, and does not appear to furnish mucic acid. Its solution dissolves calcic hydrate, and the liquid becomes yellow on standing some time, or immediately on heating; sodic and potassic hydrate have a similar action. Arabinose has a somewhat higher cupric oxide reducing power than sucrodextrose, one molecular proportion reducing 5·5 molecular proportions of cupric sulphate. It does not ferment in contact with beer yeast.

Scheibler found the apparent specific rotatory power of arabinose from sugar-beet arabin in a solution containing 10 grams in 100 cc., which had the sp. gr. 1·0381 at 15° (59° F.), to be $[\alpha]_j = +118^\circ$; the values obtained for a specimen from gum arabic were slightly different,—probably owing to a difference in the temperature, which considerably affects the rotatory power—viz., 121° for the freshly prepared solution, and 116° after standing or heating.

(1561) **Sorbinose**; *Sorbin:* $C_6H_{12}O_6$.—Sorbin was first described in 1852 by Pelouze (*Ann. Chim. Phys.* [3], xxxv. 222), who obtained it from the fermented juice of Mountain Ash berries (*Sorbus aucuparia*). The juice expressed from berries gathered towards the end of September was allowed to remain for thirteen or fourteen months in stoneware pans, during which time a considerable development of fungoid growth took place; the clear liquid was then decanted, and evaporated to a thick syrup, and the crystals which were deposited purified by recrystallization with the aid of animal charcoal.

Delffs has observed (*British Association Report*, 1871) that no sorbin is obtained if the malic acid which exists in the juice be first removed, although it is readily procured when Pelouze's process is strictly followed; moreover, no malic acid is found in the fermented juice, and Delffs, therefore, supposes that sorbin is formed during the fermentation, and that there is an intimate connexion between its formation and the disappearance of the malic acid. We may regard this, however, as doubtful.

It crystallizes in transparent, very regular, rhombic octahedra. The crystals are hard and grate between the teeth; they are as sweet as cane sugar. Water dissolves about double its weight of sorbin, but it is almost insoluble in alcohol even when boiling. Its apparent specific rotatory power in a solution containing about 30 per cent. at 7° (44°·6 F.) is − 46°·9; it appears to be only slightly variable with the temperature, and just as great in a recently prepared solution as in one that has been kept (Berthelot). It forms a compound with sodic chloride crystallizing in cubes. It may be heated to fusion without loss of weight, but on heating it to 150°—180° (302°—356° F.) water, which is slightly acid, is given off, and it is converted into a dark red mass, insoluble in water, alcohol, and the weaker acids, but readily soluble in alkalies; according to Pelouze, this residue principally consists of an acid of the composition $C_{16}H_{21}O_{9}$. Sorbin is very readily altered by alkalies, even very dilute solutions becoming yellow when warmed with potassic hydrate; its solution dissolves a considerable quantity of calcic hydrate; it is not precipitated by basic plumbic acetate, but yields a white precipitate with an ammoniacal solution of the normal acetate. It is not in the least altered by boiling with dilute acids; it is coloured reddish-yellow by cold concentrated sulphuric acid, and charred on heating. It precipitates cuprous oxide from an alkaline cupric solution, but its cupric oxide reducing power has not been determined. Sorbin does not ferment in contact with beer yeast, but is capable of undergoing the lactic fermentation (Berthelot). According to Dessaignes (*Ann. Chem. Pharm. Supp.*, ii. 242) sorbin yields aposorbic acid, $C_5H_8O_7$, together with the three modifications of tartaric acid—dextrotartaric acid, racemic acid, and mesotartaric acid, on oxidation with nitric acid; Pelouze obtained oxalic acid only. Hlasiwetz and Habermann state that on passing chlorine into an aqueous solution, and afterwards saturating with argentic hydrate, &c., it is converted into glycolic acid; it is remarkable that sorbin and lævulose, which are the only two lævorotatory glucoses at present known, should both yield glycolic acid when thus treated, especially as they are the only carbohydrates hitherto examined from which it has been obtained.

(1562) EUCALYPTOSE; *Eucalyn*: $C_6H_{12}O_6$.—Little is known of this carbohydrate. It is obtained by fermenting melitose, an isomeride of cane sugar, with yeast; apparently the melitose is thus in the first instance resolved into eucalyptose and a second glucose, of which the latter alone is fermentable, so that when the fermentation is complete the solution contains only eucalyptose, and the alcohol produced from the glucose, which disappears. It is mixed with four or five vols. of alcohol, and, after filtering, evaporated to a syrup, which is then exposed over sulphuric acid in vacuo. Eucalyptose is thus obtained as a slightly sweet syrup of the composition $C_6H_{12}O_6 + OH_2$, which loses a molecule of water on heating to 100° (212° F.); if it be heated to 110° (230° F.) it becomes coloured, and at 200° (392° F.) is converted into a black, insoluble substance. It is dextrorotatory, having approximately the apparent specific rotatory power $[\alpha]_j = 65°$. It reduces an alkaline cupric solution. Nitric acid converts it into oxalic acid. It is decomposed by concentrated sulphuric acid, or by fuming hydrochloric acid at 100° (212° F.); and when heated with baric hydrate at 100° (212° F.) the solution becomes strongly coloured (Berthelot, *Ann. Chim. Phys.* [3], xlvi. 72).

(1563) *Glucoses which have been Artificially Produced.*—According to Gorup-Besanez (*Ann. Chem. Pharm.*, cxviii. 257), when a mixture of one part mannitol and two parts platinum black, moistened with water, is exposed to the air at a temperature of 30°—40° (86°—104° F.), and the water constantly replaced as it evaporates, until the mannitol entirely disappears, which with quantities of 20—30 grams takes place in about three weeks, a product is obtained which furnishes a colourless, strongly acid solution. The acid (mannitic acid, p. 558) may be separated by the addition of basic plumbic acetate, and if, after removing the dissolved lead by sulphuretted hydrogen, the solution be evaporated at first on the water bath, and then, directly it becomes coloured, by exposure over sulphuric acid in vacuo, a pale yellow, strongly acid syrup is obtained, which gradually dries to a gum-like hygroscopic mass. This residue consists of a fermentable body, having all the characters of dextrose, with the exception that it is *optically inactive*, mixed, however, with a substance from which it could not be separated, and which is, perhaps, mannitan, $C_6H_{12}O_5$. The cupric oxide reducing power of 100 pts. of the residue was equal to that of 32·45 pts. dextrose, and another 100 pts. gave an amount of carbonic anhydride on fermentation corresponding to 32·68 per cent. of dextrose. Gorup-Besanez terms the optically inactive glucose formed in this manner *mannitose*.

Dulcitol, the isomeride of mannitol, according to Carlet (*ibid.*, cxvii. 143), also yields a body having the properties of glucose, together with a small quantity of racemic acid, on oxidation with nitric acid.

According to Berthelot (*Ann. Chim. Phys.* [3], l. 369), a body having the properties of the glucoses is sometimes formed by the fermentation of aqueous solutions of glycerol and mannitol in contact with certain nitrogenous animal substances, but the conditions necessary always to insure its production could not be ascertained. The only substance which was found to be at all regular in its action was the membrane of the testicle. This was added, in a finely divided state, to a solution of 1 pt. glycerol or mannitol in 10 pts. water, the amount taken (of the substance supposed dry) being about 1-20th of the weight of the glycerol or mannitol; the mixture, contained in an open flask, was exposed to diffused daylight at a temperature between 10° and 20° (50° and 68° F.), and the liquid occasionally tested with Fehling's solution. After an interval varying from a week to three months it was found to contain a body capable of reducing cupric solution, and of at once fermenting when placed in contact with beer yeast. Experiments with dulcitol gave similar results. The animal substance separated from the liquid, and freed from glycerol or mannitol by washing, retained, as a rule, the property of converting these compounds into the supposed glucose. The amount formed is extremely variable: in some cases being equal only to a few ten-thousandths of the weight of glycerol or mannitol taken, and in others to as much as a tenth of their weight, the latter quantity being never exceeded, however; the weight of glycerol or mannitol which disappeared was always greater than the weight of "glucose" formed. In an experiment cited by Berthelot, 2 grams of the fresh testicle, representing ·280 grams dry substance, 5 grams mannitol, and 50 grams water, gave, after an interval of nearly four months, ·250 grams of the "glucose." The animal matter, after washing and drying, weighed ·230 grams, and had therefore lost ·050 grams; but this loss is more apparent than real, as the fresh testicle contains a certain amount of soluble matter. From this it appears that the "glucose" is really derived from the mannitol, and is not precontained in, or derived from, the animal substance. Berthelot attributes its formation to a species of contact action exercised by the nitrogenous matter, and not to the microscopic organisms which are developed in the liquid; Pasteur's researches on fermentation, however, render this explanation extremely improbable, and it is far more likely that the nitrogenous matter serves merely as a pabulum for the organisms which excite the fermentation. These organisms are doubtless derived from the atmosphere, and the want of success which attended many of Berthelot's experiments may have been due, either to the non-introduction of the proper germs, or to the fact that the liquid was not suited to their development. As to the properties of the "glucose" formed, Berthelot states that it could not be obtained crystallized, and that it is extremely soluble in water and aqueous alcohol; its solutions alter very readily during concentration, and are browned by alkalies. On account of the difficulty of obtaining colourless solutions, it was almost impossible to ascertain whether it was optically active, but on one occasion it was observed that a solution containing about 1-20th of the "glucose" produced a deviation of 5°·5 for the transition tint in a column 200 mm. long.

Löwig (*Jahresb.*, 1861, 600) supposed that the portion of the product of the action of sodium amalgam on ethylic oxalate which remained after extracting the ethylic desoxalate (q.v.) by ether, contained a "fermentable sugar," but according to Brunner (*Deut. chem. Ges. Ber.*, iii. 974) this is not the case.

Lastly, we have to notice the formation of a body capable of reducing an alkaline cupric solution, but apparently not fermentable in contact with beer yeast, on boiling the so-called dioxymethylene—the polymeride of formic aldehyde (q.v.)—with lime water (Butlerow, *Ann. Chem. Pharm.*, cxx. 295): the colourless solution of this substance in lime water becomes at first yellow, and finally brownish-yellow when boiled. its characteristic odour disappearing entirely, and giving place to a caramel-like odour; no gas is evolved. If the lime water be added gradually to the boiling liquid until the coloration is observed, a neutral liquid is obtained, which is not precipitable by carbonic anhydride; and if this be concentrated on the water bath, and then exposed over sulphuric acid in vacuo, there remains a mixture of a yellow syrup and crystals of calcic formate. On treatment with absolute alcohol, the former dissolves, and after removal of the alcohol, forms an uncrystallizable sweet syrup. The composition of this body was not accurately determined, but apparently it contains proportionally less oxygen than the carbohydrates; and inasmuch as it is formed from a body which probably has the composition $C_3H_6O_3$, if formic acid is the complementary product and not the result of secondary reaction, it appears probable that it does not contain six, or some simple whole multiple of six, atoms of carbon, and therefore that it does not belong to the class of carbohydrates. Methylenitan, as this body is termed, apparently also does not exhibit one of the most characteristic properties of the soluble carbohydrates—that of forming metallic derivatives, for although obtained by the action of lime water, it gave only a small quantity of ashes on incineration, and this Butlerow attributes to the presence of calcic formate.

From the above it will be evident that our knowledge of artificially prepared glucoses is practically nil. We have entered thus fully into an account of what has been done in order to point out the great necessity of further research, for we may confidently expect that by working in this direction much light will be thrown on the manner in which the carbohydrates are naturally produced.

II. *Carbohydrates of the Composition* $C_{12}H_{22}O_{11}$ *or Saccharons.**

The carbohydrates which are included in this group are all of the same empirical composition as cane sugar, $C_{12}H_{22}O_{11}$. They are all soluble in water, and with few exceptions crystallize with facility when pure; like the glucoses, they are more or less sweet to the taste, but they are much more stable than the glucoses or carbohydrates of the composition $C_6H_{12}O_6$, and are not directly fermentable; when submitted to the action of certain "unorganized ferments" (a cold aqueous decoction of yeast, or of malt, &c.), or of dilute acids, they are more or less readily converted into glucoses, a single molecule always yielding two molecules of glucose: the two molecules of glucose being sometimes identical, but more often exhibiting diverse character. This conversion of a molecule of a saccharon into two molecules of a glucose, or into two different glucoses, necessarily involves the assumption of the elements of a molecule of water, and is indicated generally by the equation:*

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* On account of their great importance, and especially now that so many carbohydrates are known, it appears highly desirable to have a systematic nomenclature enabling a distinction to be made between the various groups; a description of the system we have ventured to employ will be given later on when the various carbohydrates have been noticed.

$$C_{12}H_{22}O_{11} + OH_2 = C_6H_{12}O_6 + C_6H_{12}O_6.$$

(1564) SACCHARON OR CANE SUGAR; *Saccharose* or *Sucrose:* $C_{12}H_{22}O_{11}$.—This sugar is very widely distributed throughout the vegetable kingdom, occurring sometimes alone, but more frequently mixed with invert sugar; it is met with in all parts of plants: in the root, stem, leaves, flower, fruit, and seed, but is not distributed in all plants alike, and occurs in proportions which vary for each plant with its state of growth. It is very abundant in the stem of certain grasses, especially in the sugar cane (*Saccharum officinarum*), sorgho grass (*Sorghum saccharatum*), and the young shoots of maize (*Zea mays*). It is also abundant in many fleshy roots, as those of the carrot and parsnep, especially in the sugar beet (*Beta vulgaris*); and also in the juice from the stems of many kinds of palm, and of certain species of birch and maple, especially the sugar maple. It is manufactured almost exclusively from the sugar cane and sugar beet.

Manufacture of Cane Sugar from the Sugar Cane.—The sugar cane is a solid jointed reed which grows to a height varying from six to fifteen feet. It is found advantageous to cut the canes before they are allowed to flower, as the produce of sugar is much reduced after inflorescence, and as close to the soil as possible, since the juice contained in the lowest joints is the sweetest; according to Peligot, no uncrystallizable (invert sugar) is contained in the fresh juice of sound canes, though it occurs in decayed ones, but Icery, who has specially studied this subject in the Mauritius, finds that even sound canes contain a small proportion of invert sugar (*Ann. Chim. Phys.* [4], v. 387). The canes stripped of their leaves are crushed between rollers, and the expressed juice is run off to a large tank, where it is neutralized by lime, and heated till the scum formed by the coagulation of the albuminous matters in the juice, and which rises to the top, begins to crack. After a time, the clear liquid is drawn off from below the scum, and concentrated by boiling in open copper pans, the impurities which rise to the surface being removed by frequent skimming. When the syrup has acquired sufficient consistence, it is run into coolers, and allowed to stand till sugar no longer crystallizes out; the same solid mass is then put into casks furnished with perforated bottoms to allow the syrup to drain away. The moist, yellowish, granular mass remaining in the casks forms the raw sugar of commerce, which consists of crystals of nearly pure sugar, coated on their surfaces with a film of the dark syrup. By reboiling the syrup which drains from the crystals, a lower quality of sugar is obtained; the last mother liquors, which are known as molasses or treacle, are thick, brown, and refuse to crystallize, and are used chiefly for the manufacture of rum.

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* The decomposition of the saccharons in this manner is usually termed inversion, and the product is spoken of as invert sugar; this arose from the observation that when cane sugar, which is dextrorotatory, is thus decomposed, it furnishes a product which exerts a lævorotatory action on polarized light in consequence of the lævorotatory power of the lævoglucose produced being considerably greater than the dextrorotatory power of the dextroglucose, which is the complementary product of the reaction.

Much waste is incurred in the extraction of sugar, for according to Dumas 100 pts. of fresh canes contain 90 pts. of juice, and of this 18 or 20 pts. are pure sugar, but on an average, one gallon of juice furnishes only one pound of sugar, or one-tenth of its weight. Much of the waste arises from the conversion of the crystallizable sugar into treacle or uncrystallizable syrup by the high temperature and frequent boilings to which it is subjected; but this is almost entirely prevented by the use of Fryer's "concretor." Although, however, great improvements have during late years been effected in the apparatus for boiling down syrups, they have not yet been adopted to any very great extent by the manufacturers of raw sugar.

Manufacture of Sugar from the Sugar Beet.—The manufacture of sugar from this root was called into existence by the wars of Napoleon, during which the ordinary supply of the article was cut off from the French. So rapidly has it grown, however, that of the 3,278,000 tons of sugar estimated to have been produced in 1873, no less than 1,110,000 tons were derived from the sugar beet. The beet is chiefly cultivated for this purpose in France and Germany, although large quantities are grown in other parts of Europe; it contains on an average from 7—11 per cent. of sugar, and sometimes as much as 14 per cent. The oldest and still most general method of extracting the juice from the roots is to reduce them to a fine pulp, which is then submitted to powerful pressure; or sometimes, however, the pulp is thrown into a centrifugal machine, and when most of the juice is expelled, water is added to the residue, and the machine again set in action. The exhausted pulp is either employed while fresh as food for cattle, or used as manure for the land. A more modern method now largely coming into use, which is known as the diffusion process, consists in cutting the roots into slices, and submitting these to systematic washing: the water which has been for some time in contact with one portion of roots, and which has dissolved a certain amount of sugar, being run on to a fresh portion of roots, while its place is taken by fresh water, four to six changes being made in this manner, the solution which has been in contact with one portion of roots being always transferred to a less exhausted portion, so that it continually undergoes concentration. The great advantage of this process is that it yields a solution comparatively free from albuminoid and gummy matters, as these cannot pass by diffusion out of the unbroken cells, although the sugar readily penetrates through their walls.

The juice is run into tanks, where it is moderately heated by steam, and mixed with a certain quantity of lime, varying from ½ to 3 lbs. for each 100 lbs. of roots taken; the mixture is then further heated until the scum breaks, the clear liquid from below the scum is drawn off into another tank, and carbonic anhydride is pumped into it until the lime in solution is nearly all precipitated. By heating with lime in this manner a number of impurities are removed from the juice, and others are precipitated with the calcic carbonate. The "thin" syrup is now filtered through animal charcoal, and boiled down in a partial vacuum to about 20° Beaumé, when it is again filtered through animal charcoal, and finally concentrated to the crystallizing point in a vacuum apparatus. The crystals which form on standing are separated from the syrup by the aid of the centrifugal machine, and by boiling down the syrup, &c., a second and third crop of crystals is obtained; finally nothing remains but uncrystallizable molasses. In France, a good deal of the molasses, which is inferior to that of the cane, is fermented, and furnishes a considerable quantity of spirit, amounting in weight to nearly one-third of the treacle employed. After distilling off the spirit, the residue is evaporated to dryness, and then incinerated for the sake of the salts it yields, which consist principally of potassic and sodic carbonates with a small proportion of potassic sulphate and chloride; by this means, the large proportion of soluble saline matters which beet root contains is economized.

Refining of Cane Sugar.—Raw cane sugar, although often mixed with mechanical impurities, has a pleasant taste; but the raw sugar from beet has a strong, unpleasant odour, and is uneatable. The same method is followed in refining both varieties. The raw sugar is first "melted," *i.e.*, dissolved, in about half its weight of water, by the aid of heat and agitation, and the hot liquid is then transferred to a filtering apparatus consisting of a number of twilled cotton bags, called Taylor's filters, where it is freed from mechanical impurities. The reddish syrup which has run through the filters has next to be freed as much as possible from colouring matter, and for this purpose it is filtered through animal charcoal. The filters consist of large iron vats, twelve or fourteen feet deep, and sometimes much deeper; at an inch or two from the bottom there is a perforated false bottom, upon which a blanket is spread, and above this coarsely powdered animal charcoal to within about a foot of the top of the vat. The filtered decolorized syrup is now boiled down, but as the cane sugar quickly undergoes inversion at the temperature at which so concentrated a solution boils under the ordinary pressure (220°—230° F.), it is evaporated under reduced pressure in a *vacuum pan.* This is a closed pan or boiler of copper, constructed of a spheroidal form, in order to enable it to resist the pressure of the external atmosphere; the lower half is double, for the purpose of admitting steam between the coatings, and there are several helices of copper steam pipe within the boiler, with a view of increasing the extent of heating surface. It is connected by a wide copper neck with a condenser, which is in communication with an air pump, and it is also provided with an inlet for the syrup which is to be boiled, and there is an outlet, which can be closed by a valve, at its lowermost part for the withdrawal of the charge. The boiling can be watched through a small plate-glass window in the side of the pan, and there is also an arrangement by which a sample of the syrup can be withdrawn at any moment. A partial vacuum being established, a cock is opened and sufficient of the filtered decolorized syrup sucked in to cover the bottom steam coil, in which steam is then turned on. In a few minutes the liquid is seen to boil, and the exhaustion is so regulated that this takes place at about 130°—140° F. The evaporation is continued until the workman in charge of the pan judges that the solution is sufficiently concentrated, which he ascertains by placing a drop between his thumb and finger, and drawing it out to a thread: the desired concentration being reached in the case of a good sugar solution when it gives a thread at least three-quarters of an inch long. A small quantity of the unboiled syrup is then sucked in, which soon causes crystals to separate from the supersaturated solution in the pan, and when crystals have ceased to deposit, fresh syrup is drawn in and boiled down as before: the sugar in this fresh portion of syrup, however, as the solution is concentrated, is mostly deposited on the crystals already formed. In this manner fresh quantities of syrup are drawn in at intervals, and concentrated, until the pan is fully charged, after which the heating is continued for a certain length of time, which varies according to the form of sugar it is desired to produce. The size of the crystals eventually obtained mainly depends on the quantity at first formed, being larger the fewer there are at the beginning. If loaf sugar is to be made, care is taken to produce only small crystals, and when the pan is fully charged its contents are heated to about 170°—180° F., either in the pan itself, or in a separate heater, and the hot mixture of crystals and syrup is then transferred to conical iron moulds. After stirring the mass to favour the escape of air bubbles, and the regular settlement of the crystals, the whole is left at rest for at least twelve hours, during which time the crystals settle down, and as the liquor cools fresh sugar is deposited and firmly cements them together. The plug which closes the aperture at the apex of the mould is then withdrawn, and a pricker driven a few inches into the solid sugar to make a channel for the syrup to drain away; the sugar, however, is not yet white, for though the crystals consist of colourless sugar, the loaves retain mechanically a large quantity of coloured syrup. In order to get rid of this, a quantity of fine colourless syrup is poured upon the base of each loaf, which gradually displaces the impurities as it percolates through the loaf. The loaf is finally dried in a heated chamber, and finished for the market by turning it in a lathe. The sugar so made is almost absolutely pure.

The syrup which drains from the loaves is boiled down again in the vacuum pan, and is obtained in the form of what is termed *crushed sugar* or *pieces*, which is freed from the syrup by means of a centrifugal machine. This syrup is again treated in a similar manner, and yields a still less pure sugar, the syrup from which constitutes refiners' molasses, or treacle.

In the manufacture of cane sugar in large distinct crystals, the crystallization of the first portion of syrup boiled down in the pan is so regulated as to form only a relatively small number of crystals, and the subsequent boilings are carried on at a somewhat higher temperature and more slowly than when loaf sugar is to be made. The crystals are freed from syrup by a centrifugal machine, and are sometimes washed with a small quantity of water while the drum of the machine is still revolving.

Refiners' treacle still contains a considerable amount of cane sugar, amounting to about 35 per cent. when made from sugar cane, and to as much as 50 per cent. when made from beet; this is prevented from crystallizing mainly by the presence of the impurities derived from the raw sugar. That from colonial sugar also contains a large amount (about 30 per cent) of invert sugar, from which that prepared from beet is comparatively free; the latter, however, is very rich in saline matters, yielding from 12—13 per cent. of ashes, whereas average refiners' treacle from raw sugar-cane sugar yields only about half as much. The beet treacle is also considerably the richer in organic matters other than cane and invert sugar. The salts of potash, which are largely contained in the treacle, exercise great influence in preventing the crystallization of the sugar, and their removal from the syrup is therefore of importance. Messrs. Duncan and Newlands have recently patented a process for this purpose, based on the fact that alum is but slightly soluble in cold syrup. It consists in adding to a cold concentrated solution of raw sugar, or of a syrup containing not less than 1·5 per cent. of potash, a sufficient amount of a strong solution of aluminic sulphate to convert all the potash present into sulphate, and to combine with the potassic sulphate so formed. On standing, the alum crystallizes out. The clear liquor, which is strongly acid, and which contains much alumina in solution, is drawn off and neutralized with lime or chalk, boiled, filtered, and then again filtered through animal charcoal in the usual way. This process reduces the potash present to about one-half per cent. on the weight of the syrup, but it has the additional advantage of removing nitrogenous matters from the solution, as these are carried down with the alumina precipitated on neutralization.

Cane sugar crystallizes from a concentrated aqueous solution on slow evaporation in large colourless monoclinic prisms, generally with hemihedral faces; the crystals are hard, and grate between the teeth. It has a sp. gr. of about 1·6.* It dissolves in less than half its weight of water at ordinary temperatures, and still more easily in hot water, forming a syrupy liquid; but it is insoluble in ether and cold anhydrous alcohol, and only slightly soluble in anhydrous boiling alcohol.

The apparent specific rotatory power of cane sugar in aqueous solution is variously stated, but the most reliable observations with solutions containing from 10 to 20 per cent. of sugar give the values $[\alpha]_j=73^{\circ}$—$73^{\circ}{\cdot}8$. According to De Luynes and Girard, however, it is slightly higher—viz., for a solution containing about 16 per cent. by weight, $[\alpha]_D=67^{\circ}{\cdot}31$, hence by calculation $[\alpha]_j=74^{\circ}{\cdot}04$ (comp. Tollens, *Deut. chem. Ges. Ber.*, ix. 493). Calderon (*Compt. Rend.*, lxxxiii. 393) has obtained the values $[\alpha]_D=67^{\circ}{\cdot}15$ and $[\alpha]_j=73^{\circ}{\cdot}20$, both by direct observation. Apparently it is independent of the temperature (Tuschmidt, *Journ. pr. Chem.* [2], ii. 243); and it is usually supposed that it does not vary with the concentration, but this does not appear to have been established by an exact series of experiments (comp. Hesse, *Ann. Chem. Pharm.*, clxxvi. 95). The rotatory power of a freshly prepared solution is not altered by standing or by heating.

Cane sugar melts at about 160° (320° F.) to a clear liquid, and on cooling forms the transparent amber-coloured solid sold as *barley-sugar*, which gradually becomes opaque and crystalline when kept: this amorphous sugar has a much lower melting-point than the crystalline modification. If the temperature be maintained for some time at about the melting-point, the sugar is converted without loss of weight into a mixture of sucrodextrose and lævulosan: $C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$. At a higher temperature water is given off, the dextrose apparently undergoing alteration, and at about 210° (410° F.) so-called *caramel* is produced, which probably is a mixture of several bodies formed by the withdrawal of the elements of water from the dextrose and lævulosan; it is a brown, very hygroscopic, almost tasteless mass. On further heating, an inflammable gaseous mixture is given off, consisting of carbonic oxide, carbonic anhydride, and methane, and a distillate is obtained containing acetic acid, aldehyde, acetone, furfurol, and other substances not yet identified, whilst a porous, glistening, carbonaceous mass remains in the retort.

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* Cane sugar in solution has the sp. gr. 1·626 at 15°·5 (60° F.), as may be calculated in the following manner. A solution of 10 grams sugar in 100 cc. at 15°·5 (60° F.) has at this temperature the sp. gr. 1·0385; the weight of water in 100 cc. of the solution is therefore 103·85 − 10 = 93·85, and hence the volume occupied by the 10 grams sugar is 100 − 93·85 = 6·15, and the sp. gr. of the sugar 10 ÷ 6·15 = 1·626. O'Sullivan finds that sucrodextrose, invert sugar, maltose, dextrin, and soluble starch have the same sp. gr. as cane sugar in solution; and it is therefore not unlikely that this will be found to be the case for the carbohydrates generally. This fact is of considerable practical importance as the amount of solid matter in a solution of carbohydrates may be ascertained if the sp. gr. at 15°·5 (60° F.) be determined by merely dividing the weight above water by ·00385. The most complete tables of the densities of aqueous solutions of cane sugar of different strengths have been published by Mategczeck: *Zeitschrift des Vereins für Rübenzucker-Industrie*, 1865, 583; 1874, 843; Scheibler: *ibid.*, 1870, 269; 1874, 950; and Gerlach: *ibid.*, 1863, 283; 1864, 354; 1865, 23. The solubility of sugar in alcohol of different strengths and at different temperatures has been carefully determined by Scheibler (*Deut. chem. Ges. Ber.*, v. 343).

A number of metallic derivatives of cane sugar are known, but their composition is not yet satisfactorily established; although much more stable than the corresponding derivatives of the glucoses, they are decomposed even by carbonic acid. Thus, on adding a concentrated solution of potassic or sodic hydrate to an alcoholic solution of sugar, white gelatinous precipitates, $C_{12}H_{21}KO_{11}$ and $C_{12}H_{21}NaO_{11}$, are thrown down; and on mixing concentrated solutions of baric hydrate and of sugar, a crystalline precipitate is obtained, having the composition $C_{12}H_{22}BaO_{12}$, which may be recrystallized from boiling water, separating from it in brilliant scales resembling crystallized boric acid. Again, calcic hydrate is far more soluble in a sugar solution than in pure water. According to Peligot, the compound $C_{12}H_{22}CaO_{12}$ is thrown down from a solution containing not too much lime, on the addition of alcohol, as a white precipitate which dries to a gum-like resinous mass; Benedikt (*Deut. chem. Ges. Ber.*, vi. 413) has prepared this compound in a similar manner, and states that after drying at 100° (212° F.) it has the composition $C_{12}H_{20}CaO_{11}$, but that it contains $2OH_2$ in addition, if only dried in vacuo; it is extremely soluble in water, but on heating the solution it becomes turbid from the separation of the compound $C_{12}H_{22}Ca_3O_{14}$, which redissolves, however, as the solution cools. The latter compound may be prepared by boiling a solution of sugar which has been saturated with lime, separating as an opaque gelatinous mass. It is said that the dicalcium derivative, $C_{12}H_{22}Ca_2O_{13} + 2OH_2$, is precipitated from a similar solution on the addition of alcohol.*

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* According to Dubrunfaut, the rotatory power of a sugar solution is reduced by 13 per cent. if one molecular proportion of calcic hydrate, by 26 per

Judging from the behaviour of the polyhydric alcohols, such as dulcitol and mannitol, in which the hydrogen in the OH group appears to be only partially displaceable by the more positive metals, if the formulæ assigned to these calcium derivatives correctly represent their composition, it is not improbable that in their formation the hydrogen in sugar is displaced by the monad group Ca.OH, and not, as in the formation, for example, of anhydrous calcic sulphate from sulphuric acid, merely by calcium: in other words, that the calcium atoms do not displace an equivalent number of hydrogen atoms, but only half the number. The formulæ of the barium and calcium derivatives above mentioned may on this assumption be written in the following manner:

$$C_{12}H_{21}(Ba.OH)O_{11}\ ;\ C_{12}H_{21}(Ca.OH)O_{11}\ ;\ C_{12}H_{19}(Ca.OH)_3O_{11}.$$

The majority of the metallic derivatives of the carbohydrates are probably bodies of similar composition. A crystalline lead derivative, which, after drying at 170° (338° F.) in vacuo, has the composition $C_{12}H_{18}Pb_2O_{11}$, may be obtained either by boiling a solution with plumbic oxide, and allowing the filtrate to cool; or by precipitating a concentrated solution of sugar with an ammoniacal solution of plumbic acetate, dissolving the precipitate in boiling water, and allowing it to crystallize. It forms white nodules (Peligot).

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cent. if two molecular proportions of calcic hydrate be dissolved in it; on neutralizing the solution with an acid, it recovers its rotatory power, however. The solution also loses 13 per cent. of its rotatory power on addition of one molecular proportion of potassic hydrate, but no more when a larger quantity is added; hence there is probably but one definite potassium derivative of cane sugar which can exist in aqueous solution. Sostmann (*Zeits. f. Rübenzucker In.*, 1866, 82, 272) states, however, that the effect produced by the carbonate and hydrate of potassium and sodium is greater in concentrated than in dilute solutions.

According to recent experiments of Müntz (*Compt. Rend.*, lxxxiii. 1334), a large number of salts of the alkali and alkaline earth metals reduce the rotatory power of cane sugar, but in very different proportions, the most active salts being the chloride, carbonate and borate of sodium, and potassic carbonate; the salts of metals such as lead and zinc have little or no influence. In the case of sodic chloride, the presence of 2·5, 5, 10, 20, and 25 grams in 100 cc. of solution containing 10 grams sugar, was found to reduce the rotatory power from 67° to 66°·7, 66°·2, 65°·3, 63°·7, and 62°·8, and practically the same results were obtained with solutions containing five and twenty grams of sugar. Müntz has also examined the influence of lime, and finds that the addition of ·409 gram CaO to a solution of 10 grams sugar in 100 cc. reduces the rotatory power from 67° to 64°·4; that twice the amount of lime reduces it to 61°·3; three times the amount to 56°·9; and four times the amount to 54°·8. These results obviously do not agree with Dubrunfaut's.

When cane sugar is warmed with an excess of acetic anhydride, a vigorous action takes place, which, when once established, continues spontaneously; the product, after washing with water and drying, is a gum-like amorphous mass of the composition $C_{12}H_{15}(C_2H_3O_2)_7O_4$. By prolonging the action of the anhydride, an octacetate, $C_{12}H_{14}(C_2H_3O_2)_8O_3$, having similar properties, is finally obtained (Schützenberger).

Cane sugar, like sucrodextrose, combines with sodic chloride, forming the compound $C_{12}H_{22}O_{11}.NaCl.2OH_2$, which with some difficulty is obtained crystallized in prisms terminated by pyramids. It also combines with sodic iodide, the compound $2C_{12}H_{22}O_{11}.3NaI.3OH_2$, crystallizing with the greatest readiness from solutions containing a moderate excess of the iodide, in large transparent monoclinic prisms, which can be recrystallized as often as desired from water or aqueous alcohol without suffering decomposition. A solution of these crystals has the rotatory power corresponding to the amount of sugar present (Gill, *Journ. Chem. Soc.*, xxiv. 269).

Cane sugar is much less readily acted upon by alkalies than the glucoses, but on the other hand it is extremely sensitive to the action of acids. Thus, when boiled with a moderately concentrated solution of potassic or sodic hydrate, the liquid only slowly becomes of a yellow, and later on of a brown colour. If it be heated with potassic hydrate and only a small quantity of water, the mixture becomes at first brown, but is afterwards decolorized and evolves hydrogen, and then contains a large quantity of potassic oxalate. On heating it in sealed tubes to 150° (482° F.) with water and 2—3 pts. baric hydrate, it yields 70—80 per cent. of its weight of lactic acid, and small quantities of carbonic and oxalic acids, and of an acid which furnishes a zinc salt soluble in alcohol (Schützenberger, *Deut. chem. Ges. Ber.*, ix. 448). If a mixture of 3 pts. quicklime and 1 pt. sugar is distilled, a large quantity of inflammable gas is evolved, and a distillate is obtained consisting of a watery and an oily layer; the former contains acetone, together with a small quantity of acetic acid, and the latter contains *metacetone*, $C_6H_{10}O$ (B.P. 83°—84° C.), *isophorone*, $C_9H_{24}O$ (B.P. 210° C.), and bodies of higher boiling point. Probably the sugar is resolved into acetone, methane, carbonic anhydride, and water, and the metacetone and isophorone are products of condensation of the acetone (Benedikt, *Ann. Chem. Pharm.*, clxii. 303).

Cane sugar is converted by very long boiling with water into a mixture of equal proportions of sucrodextrose and sucrolævulose:* $C_{12}H_{22}O_{11}+OH_2=C_6H_{12}O_6+C_6H_{12}O_6$. This change (inversion) takes place even at ordinary temperatures in the presence of acids, especially of hydrochloric and sulphuric acids, and is almost instantaneously effected on heating a solution containing a small percentage of either of these acids to 65°—70° (149°—158° F.), and without coloration of the liquid.

The rate at which inversion proceeds depends, however, not only on the temperature, but also on the nature of the acid, and the relative amounts of sugar and acid contained in the solution.

It is more rapid the higher the temperature, but the law of variation is unknown; and the mineral acids are far more active than the organic acids, acetic, tartaric, and citric acids having but little influence at ordinary temperatures. According to Fleury (*Ann. Chim. Phys.* [5], vii. 381), at a temperature of 18°—24° (64°·4—75°·2 F.), hydrochloric acid acts more rapidly than the equivalent amount of sulphuric acid,† and sulphuric more rapidly than phosphoric acid; but arsenic acid has a greater effect than the equivalent quantity of phosphoric acid. For solutions containing the same amount of a given acid, but varying amounts of sugar, the rate of change at any moment appears to be proportional to the amount of undecomposed sugar existing in the liquid; but if the amount of sugar be the same and the amount of acid vary, the inversion does not take place at an increasing rate proportional to the increase in the amount of acid, but at a much greater rate.

Certain salts also assist inversion, but apparently this is to be attributed to the action of the acid formed by their decomposition when dissolved in water.‡ Most remarkable, however, is the influence of a cold aqueous decoction of yeast free from yeast cells and of malt extract, saliva, pancreatic juice, and many other substances of animal and vegetable origin, which rapidly effect the inversion of sugar even at ordinary temperatures, but especially at temperatures slightly higher, not exceeding blood heat; the action of these substances is due to certain unstable nitrogenous bodies which they contain, but as yet no satisfactory explanation has been given of the manner in which these "unorganized ferments," as they are generally termed, induce the decomposition of cane sugar by water.

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* The manner in which the lævulose may be isolated from the product has already been described (p. 584); the dextrose may be obtained, after removal of the acid, by evaporating the solution to a thin syrup, and allowing this to stand, when, sooner or later, crystals are formed, which may be purified in the manner we have described when speaking of the preparation of sucrodextrose from honey.

† It has been stated that sulphuric acid acts more rapidly than hydrochloric acid.

‡ In order to test the theory that certain salts undergo decomposition when dissolved in water, Fleury has compared the effect of several salts on the inversion of cane sugar solutions with that of the corresponding acids, and has obtained results of considerable interest. In an experiment with hydric potassic sulphate, $KHSO_4$, he found that the influence of this salt was only equal to that of about 1-10th the quantity of acid which would be formed supposing it were entirely converted on solution, into sulphuric acid and normal potassic sulphate; similarly, the action exercised by aluminic sulphate was equal to less than 1-50th part of that of the sulphuric acid equivalent to the amount of salt taken. Quinine sulphate and hydrochloride, morphine hydrochloride, and a mixture of sodic acetate with the equivalent amount of hydrochloric acid, were entirely without action; this last observation is of interest as a further proof that a salt like sodic acetate is entirely decomposed when a strong acid, such as hydrochloric acid, is added to its solution. A more extended series of observations according to this method would be of considerable value.

The inversion of a cane sugar solution is attended with a contraction in volume (comp. Chancel, *Compt. Rend.*, lxxiv. 876), and also with development of heat (Fleury, *loc. cit.*, p. 404). There is also an increase in the specific gravity of the liquid: thus, a solution containing at 15°·5 (59°·9 F.) 10 grams cane sugar in 100 cc. has at this temperature the sp. gr. 1·0385, but a solution of the invert sugar from 10 grams cane sugar (10·526 grams) in 100 cc. has the sp. gr. 1·0405. Moreover, as the inversion proceeds, the dextrorotatory power of the liquid gradually diminishes, and at a certain point the solution is apparently optically inactive, but it soon begins to exhibit lævorotatory action: this, as we have already stated, is because the lævorotatory action of sucrolævulose is much greater than the dextrorotatory action of sucrodextrose—viz., in about the proportion of 106 : 58 at 14° (57°·2 F.). For example, a solution of 16·19 grams cane sugar in 100 cc. requires for compensation 100 divisions of the Soleil-Duboscq scale, but to compensate after its inversion, if the reading be taken at 0° (32° F.), it is necessary to shift the scale about 44 divisions from the zero point in the opposite direction.*

It is important to notice that the mixture of dextrose and lævulose formed on inversion is liable to change if the heating be continued after the inversion is complete; indeed, O'Sullivan finds (*private communication*) that if heated for a considerable length of time, the solution not only becomes slightly coloured, but its sp. gr. increases, while its optical activity and cupric oxide reducing power diminish. Thus, the sp. gr. of the solution of the invert sugar from 10 grams cane sugar in 100 cc. being 1·0405, and its specific rotatory power calculated on the total matter in solution $[\alpha]_j = -22°·8$, he observed an increase of the sp. gr. to 1·0430,—which is equivalent to 11·17 grams of solid matter in the 100 cc.—and at the same time the specific rotatory power was reduced to $[\alpha]_j = -12°·7$, and the cupric oxide reducing power diminished from 105·26 to 85—90. It would appear, therefore, that either the dextrose or lævulose, or perhaps both, undergo further hydration; the nature of the body or bodies which are formed has yet to be ascertained, but from preliminary experiments, O'Sullivan believes that the product does not reduce an alkaline cupric solution, neither is it fermentable.*

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* As the apparent specific rotatory power of sucrodextrose is known, we may readily calculate that of sucrolævulose from the observation of the rotatory power of a solution of invert sugar. For example, a solution of 10·526 grams of invert sugar in 100 cc. is found at the ordinary temperature to have the specific rotatory power $[\alpha]_j = -22^\circ{\cdot}8$, but as only one-half the matter in solution exercises lævorotatory action, this number must be doubled, and therefore becomes $-45^\circ{\cdot}6$; obviously to this must now be added the apparent specific rotatory power of sucrodextrose—viz., $[\alpha]_j = 58^\circ$ (about), and we thus obtain the value $[\alpha]_j = -103^\circ{\cdot}6$ as the apparent specific rotatory power of sucrolævulose.

Grote and Tollens have shown (*Ann. Chem. Pharm.*, clxxv. 181) that if a more concentrated sulphuric acid solution be employed, the invert sugar, or rather principally one of its constituents—the lævulose—undergoes still more profound change. Thus, if a mixture of 400 grams cane sugar, 400 grams sulphuric acid, and 4300 grams water be heated to boiling during several days, a considerable amount of black humus-like matter separates, and the solution contains formic and lævulinic acids, together with humus-like substances and sucrodextrose. Lævulinic acid, $C_5H_8O_3$, below 11° (51°·8 F.) crystallizes in scales resembling crystallized acetic acid; it is monobasic, and furnishes a series of crystalline salts, of which the silver salt is the most characteristic. It boils at about 260° (500° F.); water dissolves it in all proportions, and the solution is optically inactive; when heated at 100° (212° F.) with a 5 per cent. solution of sulphuric acid it is but little affected. On treating dextrose in a similar manner, very little of the humus-like matters were formed, and neither formic nor lævulinic acid could be separated from the solution; but lævulose from inulin furnished a considerable amount of humus, and both formic and lævulinic acids, so that there can be no doubt that the latter are derived from sucrolævulose, and not from sucrodextrose. Their formation may be empirically represented by the equation:

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* A crystalline body which after drying in the air has the composition $C_6H_{14}O_7$ has been isolated from refiners' molasses by Loiseau (*Compt. Rend.*, lxxxii., 1058). *Raffinose*, as this substance is termed, is almost destitute of sweet taste; at 20° (68° F.) it dissolves in about 7 pts. of water, but in all proportions in hot water; the solution has a higher dextrorotatory power than that of cane sugar in the proportion of 100 : 159, hence $[\alpha]_j = 117°$. It melts at about 80° (176° F.), and when heated to 100° (212° F.) loses 15·1 per cent. water, which it regains in great part when exposed to moist air; the residue has therefore the composition represented by the empirical formula $C_6H_{10}O_5$.

The observations of Müntz and of Girard and Laborde (*Compt. Rend.*, lxxxii) also indicate that the syrup which drains from raw cane sugar and molasses contains a substance different from invert sugar; in most cases apparently it is optically inactive, although capable of reducing Fehling's solution.

$$\underset{\text{Sucrolævulose.}}{C_6H_{12}O_6} = \underset{\text{Lævulinic acid.}}{C_5H_8O_3} + \underset{\text{Formic acid.}}{CH_2O_2} + OH_2.$$

Concentrated sulphuric acid very readily decomposes cane sugar, vapours of formic acid and sulphurous anhydride and carbonic oxide being evolved, while a voluminous black carbonaceous mass remains; but it is stated that if it be very carefully mixed with the cold acid, it becomes brown without evolving sulphurous anhydride, and the mixture is completely soluble in water without separation of carbon. Concentrated hydrochloric acid also acts violently on cane sugar and chars it.

If heated with alcohol to 160° (320° F.), cane sugar remains unaffected, but water at this temperature decomposes it, about half its carbon being separated as carbonic anhydride and in the solid state, whilst the solution contains formic acid (Loew); according to Gorup-Besanez, if it be heated with water to 280° (536° F.), a very large quantity of carbonic anhydride and of black carbonaceous matter is formed, and also a small amount of pyrocatechol.

Cane sugar is readily oxidized, although as compared with the glucoses, it opposes very considerable resistance to the action of the weaker oxidizing agents. Thus, it reduces silver and mercury salts when boiled with them, and precipitates gold from a solution of the chloride, but only very slowly reduces Fehling's solution; and, like the glucoses, it dissolves cupric hydrate in presence of alkali, forming a blue solution from which cuprous oxide is precipitated on boiling. Probably, however, in all these cases the cane sugar is not directly oxidized. On careful treatment with dilute nitric acid, it yields saccharic acid, usually together with tartaric and oxalic acids which are formed from the latter by further oxidation. Dry chlorine does not attack it at ordinary temperatures, but on passing the gas into an aqueous solution of cane sugar, and subsequently neutralizing with argentic hydrate, &c., gluconic acid is obtained identical with that produced from sucrodextrose (Hlasiwetz and Habermann). When distilled with manganic peroxide and dilute sulphuric acid, it yields a considerable amount of formic acid.

As already mentioned, it is not directly fermentable, but when its dilute aqueous solution is mixed with yeast, it rapidly undergoes inversion, and the mixture of dextrose and lævulose thus formed then enters into fermentation: about 51 to 52 parts of alcohol being produced for each 100 parts of cane sugar employed.

Estimation of Cane Sugar.—The presence of cane sugar can only be satisfactorily established by quantitative analysis, if it occurs together with other bodies, and is then only possible if the foreign substances are either optically inactive and also without action on Fehling's solution both before and after inversion, or of known optical activity and cupric oxide reducing power; if this be not the case, it becomes necessary to isolate the sugar by appropriate treatment in order to be sure of its presence.

If a solution contain simply cane sugar, its amount may readily be estimated by determining the specific gravity, or the rotatory power of the solution; but this is seldom the case, the sugar as a rule occurring together with other substances, which sometimes are without action on polarized light, and do not reduce Fehling's solution, but more often either reduce Fehling's solution or exhibit optical activity, or are both optically active and capable of precipitating cuprous oxide.

The presence of cane sugar in a given substance or solution is in the highest degree probable if, when examined by polarized light, the solution of the substance, or the original solution respectively, is found to possess dextrorotatory power, but to be without immediate action on Fehling's solution, and after heating with an acid to possess lævorotatory power, and to be capable of immediately reducing an alkaline cupric solution. In order to establish the presence of cane sugar, however, it is necessary to determine the rotatory power of the solution, both before and after inversion: then, since invert sugar is a mixture of equal proportions of sucrodextrose and sucrolævulose, and the specific rotatory powers of the two bodies are respectively $[\alpha]_j = 57^\circ{\cdot}6$ and -106° (at 14° C. or $57^\circ{\cdot}2$ F.), the specific rotatory power of the mixture is $\frac{57{\cdot}6}{2} - \frac{106}{2} = -24^\circ{\cdot}2$ at 14° C. ($57^\circ{\cdot}2$ F.), and provided the observation be made at this temperature, the number of degrees of lævorotation produced by a solution of the invert sugar formed from a solution of cane sugar of arbitrary strength, but of known dextrorotatory power, is calculated by multiplying the number of degrees of dextrorotation exhibited by the cane sugar solution by ·32, since the specific rotatory power of cane sugar is $[\alpha]_j = 73^\circ{\cdot}8$ and $24{\cdot}2 = 73{\cdot}8 \times 0{\cdot}32$. If the calculated and observed values are fairly accordant, the presence of cane sugar may be regarded as established. Another method which is perhaps preferable, as it does not require a knowledge of the specific rotatory powers of the constituents of invert sugar, consists in observing the rotatory power of the original solution and its cupric oxide reducing power after inversion: from the latter value the amount of cane sugar present in a given volume or weight of the solution is readily deduced, and, this being ascertained, the apparent specific rotatory power of the substance in solution may then be calculated and compared with the known value, with which it must coincide within the limits of experimental error if the solution contain only cane sugar. The calculation is made in the following manner:—Invert sugar having the same cupric oxide reducing power as sucrodextrose, as one molecular proportion of the latter reduces five molecular proportions of cupric oxide, we have the relation:

$$C_6H_{12}O_6 : 5CuO = 180 : 396{\cdot}5;$$

but one molecular proportion of cane sugar furnishes one of dextrose and one of lævulose, so that the invert sugar from a single molecular proportion of cane sugar reduces ten molecular proportions of cupric oxide, or:

$$C_{12}H_{22}O_{11} : 10CuO = 342 : 793.$$

From this it follows that each gram of cupric oxide obtained (p. 568) represents $\frac{342}{793}$ or ·431 gram of cane sugar; hence, to find the number of grams of cane sugar c in 100 cc. of solution, we have $c = x \times 0{\cdot}431$, where x equals the number of grams of cupric oxide which would be obtained on reduction of Fehling's solution by the invert sugar formed from 100 cc. of the original solution.

The method just described obviously applies not only to the detection, but also to the estimation of the amount of cane sugar in a given solution. But the amount of cane sugar in a given substance containing no other optically active body may readily be ascertained by merely observing the rotatory power of a solution of the substance of known strength, for a solution containing in 100 cc. 16·19 grams of cane sugar produces in the Soleil-Duboscq saccharometer a displacement of 100 scale divisions:* therefore, if 16·19 grams of the given substance be dissolved in water to 100 cc., and the solution examined in this saccharometer in a tube 200 mm. long, the observation being made for the temperature at which the solution is prepared, the number of scale divisions required for compensation directly represents the percentage of cane sugar in the substance; or, if one of the other forms of apparatus illuminated by sodium light be employed, and the angular deviation produced by a solution of the above strength in a tube 200 mm. long observed, the amount of cane sugar present, y, may be calculated by the simple proportion:

$$21\cdot80 : x = 16\cdot19 : y$$

where x equals the observed angular deviation, since a solution of 16·19 grams cane sugar in 100 cc. produces in a column of 200 mm. a deviation of 21°·80. The observation may be checked by determining the rotatory power of the solution after inversion.†

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* The amount of cane sugar which, when dissolved in water to 100 cc. and the solution examined at the same temperature as that at which it is prepared in a tube 200 mm. in length, is required to produce a deviation equal to 100 divisions of the Soleil-Duboscq scale, was for the first time ascertained by Clerget in 1849, who stated it to be 16·471 grams. Dubrunfaut afterwards found this to be too high, and reduced it to 16·390 grams, which later on was still further reduced to 16·35 grams by a commission consisting of Pouillet, Barreswil, Schlösing, and Duboscq. Recently, however, De Luynes and Girard have very carefully redetermined the value of the constant in question, and find that only 16·19 grams of cane sugar are required to produce the same amount of deviation as a plate of quartz 1 mm. in thickness.

† According to Tuschmidt (*Journ. pr. Chem.* [2] 1870, ii. 235), a solution of cane sugar which before inversion produces a deviation corresponding to 100 divisions of the Soleil-Duboscq scale, after inversion, if the observation be made at 0° (32° F.) causes a deviation of 44·16 divisions in the opposite direction; but for each degree C. rise of temperature the deviation after inversion diminishes by ·505 divisions of the scale. Tuschmidt has given formulæ which enable the relation between the temperature and the deviation produced by a solution of invert sugar to be calculated for solutions of any strength, and also tables by reference to which the amount of cane sugar in a given solution may be ascertained when the deviation which it produces before and after inversion is known. These tables are based on the formula:

$$144\cdot16035 - 0\cdot50578\,t : 100 = S : R$$

$$R = \frac{100\,S}{144\cdot0635 - 0\cdot50578\,t'}$$

where R is the required percentage of cane sugar in the solution, S the *sum* of the scale readings before and after inversion, and t the temperature at which the observation is made after inversion. Calculated for the forms of instrument with which sodium light is employed, and the absolute angular deviation determined, this formula becomes:

$$R = \frac{21\cdot7189\,S}{31\cdot310 - 0\cdot10985}.$$

Another method of distinguishing whether a soluble carbohydrate which only reduces Fehling's solution after heating with dilute acid is cane sugar or not, without the employment of the polarimeter, depending on the fact that, although dextrose and lævulose have the same cupric oxide reducing power, they do not reduce all oxidizing agents to the same extent, consists in determining the cupric oxide reducing power of the solution after inversion, and also its mercuric iodide reducing power in the manner described below.* This method also enables us to determine whether a solution in which a reducing body is present contains dextrose or invert sugar only, or a mixture of both, and the proportion in which they are present. For example, it is found on the one hand that exactly 25 cc. of the solution are required to reduce ·72 grams HgI_2, and on the other that these 25 cc. reduce an amount of Fehling's solution corresponding to ·125 gram glucose, $C_6H_{12}O_6$; we therefore have the equation:

$$x + y = \cdot 125,$$

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* The mercuric iodide reducing power is ascertained by a modification of Knapp's method (p. 582), which, according to Sachsse, does not yield constant results (*Chemie d. Farbstoffe, Kohlehydrate, &c., Leipsig: L. Voss.* 1877). Knapp found that 100 pts. dextrose reduce 400 pts. mercuric cyanide, which is in the ratio of one molecular proportion of the former to somewhat less than three of the latter, as the proportion $C_6H_{12}O_6 : 3Hg(CN)_2$ requires the reduction of 420 pts. of the cyanide; but Sachsse states that the amount of cyanide reduced depends on the rate at which the dextrose is added to the boiling mercuric cyanide solution, the reduction being greater the more rapidly the titration is effected. He finds, however, that an alkaline solution of another mercuric salt—viz., the iodide, yields constant results. The solution is prepared by dissolving 18 grams pure dry mercuric iodide in water with the aid of 25 grams potassic iodide, adding to this 80 grams of potassic hydrate dissolved in water, and then diluting to 1000 cc. Of this solution, 40 cc., containing ·72 gram of mercuric iodide, are heated to boiling in a porcelain dish, and the solution of the carbohydrate of about half a per cent. strength is then added—at first in quantities of 5 cc. at a time, then in quantities of 1 cc., and lastly by tenths of a cubic centimetre, until the whole of the mercury is precipitated, which is ascertained by means of a saturated solution of commercial stannous chloride in alkali, a number of drops of which are placed on a porcelain plate, and one of them mixed with a drop of liquid from the dish after each addition of the carbohydrate solution: at first a black precipitate is formed, which becomes less and less evident as the reduction proceeds, and the titration is regarded as complete when the addition of a drop of the titrated liquid no longer produces even a brown coloration.

It is found in this manner that on an average ·1501 gram of dextrose is required to effect the reduction of 40 cc. of mercuric iodide solution containing ·72 gram HgI_2, which is in the proportion of 2.454 : 189, or nearly as $2HgI_2 : C_6H_{12}O_6$ (2.254 : 180). Invert sugar, however, has a much greater reducing power, ·1072 gram sufficing entirely to precipitate the mercury from 40 cc. of the mercuric iodide solution; from this, supposing the dextrose to have the same reducing power as when alone, we may calculate that the amount of lævulose required to reduce ·72 gram of mercuric iodide is $2 \times 0.1072 - 0{\cdot}1501 = 0{\cdot}0643$ gram, which is in the proportion of 9·454 : 364 or nearly as $2C_6H_{12}O_6 : \cdot 9HgI_2$. This remarkable difference in the behaviour of dextrose and lævulose is of the greatest interest, and it may be expected that further observations of this kind on the behaviour of the different glucoses with various oxidizing agents will furnish results of much importance.

where x is the dextrose and y the invert sugar. In order to find the second equation which is necessary to ascertain the value of these two unknowns, we have merely to bear in mind that ·1504 gram dextrose, but only ·1072 gram invert sugar is required to reduce ·72 gram HgI_2; therefore x grams dextrose correspond to $x \times \frac{\cdot72}{\cdot1501} = 4{\cdot}79\,x$ and y grams invert sugar to $y \times \frac{\cdot72}{\cdot1072} = 6{\cdot}71\,y$ grams mercuric iodide, and therefore:

$$4{\cdot}79\,x + 6{\cdot}71\,y = {\cdot}72.$$

Hence, $x = {\cdot}0618$ and $y = {\cdot}0632$; in other words, the solution contained a mixture of dextrose and invert sugar in nearly equal proportions. Obviously, if x or $y = 0$, invert sugar or dextrose only is present; in the former case, supposing the solution had been prepared from a substance which did not immediately reduce Fehling's solution, by heating it with a dilute acid, it would follow that the substance under examination was cane sugar, but if dextrose alone were present it would follow that the substance examined consisted of dextrin, or of a similar body, which yields only dextrose when boiled with acids.

This method of analysis will doubtless be found generally applicable when the behaviour of other carbohydrates besides sucrodextrose and sucrolævulose with various oxidizing agents has been ascertained.

If cane sugar occur together with invert sugar, the mixture may be approximately analysed by simply determining its cupric oxide reducing power both before and after heating with acid; the determination of cane sugar in presence of invert sugar in this manner is not exact, as the former does not entirely escape oxidation when heated with Fehling's solution, the error from this cause being greater the more slowly the titration is effected (Scheibler, *Deut. chem. Ges. Ber.*, v. 928). In order, however, to check the results of analysis, and to ascertain whether dextrose and lævulose are present in the proportions in which they occur in invert sugar, the rotatory power of a mixture of the composition ascertained by the analysis is calculated and compared with the observed rotatory power before treatment with acid. By also observing the rotatory power after treatment with acid, the actual amount of dextrose and lævulose present may even be determined; as an example of this, the following analysis of honey may be cited:—10 grams honey were treated with cold water, the solution filtered from wax, &c., then made up to 100 cc. at $15^\circ{\cdot}5$ (60° F.), and the sp. gr. determined in order to ascertain the amount of matter dissolved; the sp. gr. was found to be $1{\cdot}03115 = 8{\cdot}1$ grams solid matter in the 100 cc., or 81 per cent. soluble solid matter in the honey. The apparent specific rotatory power of the solid matter thus dissolved was found to be $[\alpha]_j = -13^\circ{\cdot}4$, the solution requiring for compensation in a 220 mm. tube -10 divisions of the Soleil-Duboscq scale, and its cupric oxide reducing power to be $= 91$.

Another stronger solution, made without weighing the honey, was heated with one or two drops dilute sulphuric acid for about an hour, the acid neutralized with baryta water, and, after removal of the baric sulphate, was diluted to 100 cc. at $15^\circ{\cdot}5$ (60° F.). Its sp. gr. was found to be $1{\cdot}04032 = 10{\cdot}472$ grams solid matter in 100 cc.; its apparent specific rotatory power, deduced from the observation that it required for compensation in the 220 mm. tube $-16{\cdot}5$ scale divisions, being $-17^\circ{\cdot}3$, and its cupric oxide reducing power $99{\cdot}5$.

From the cupric oxide reducing power it is evident that the optical activity of the solution is entirely due to the glucoses present; and, supposing that these consist of a mixture of dextrose and lævulose, we may calculate the composition of the mixture in the following manner:

Let x = dextrose; then $9{\cdot}95 - x$ = lævulose.

The apparent sp. rot. power corresponding to 1 gram dextrose in 100 cc. is $5^\circ{\cdot}76$, and to one gram of lævulose $-10^\circ{\cdot}46$; therefore

$$5{\cdot}76\,x + (9{\cdot}95 - x) - 10{\cdot}46 = -17^\circ{\cdot}3,$$

whence $x = 5{\cdot}35$ grams dextrose in $9{\cdot}95$ grams solid matter, the residue, $4{\cdot}60$ grams, being lævulose.

From the reducing power before inversion, we see that 10 grams solid matter contain $9{\cdot}1$ grams of glucoses; hence the amount of cane sugar is represented by

$$9{\cdot}95 - 9{\cdot}1 = {\cdot}85 \text{ grams invert sugar,}$$

$$\text{but 10 grams cane sugar} = 10{\cdot}526 \text{ grams invert sugar,}$$

$$\therefore\ 10{\cdot}526 : 10 = {\cdot}85 : {\cdot}845.$$

Now $\cdot 85$ gram invert sugar $= {\cdot}425$ gram dextrose and $\cdot 425$ gram lævulose,

$$\begin{array}{rcrcrcl} \therefore\ 5{\cdot}35 & - & {\cdot}425 & = & 4{\cdot}925 & = & \text{original dextrose} \\ 4{\cdot}60 & - & {\cdot}425 & = & 4{\cdot}175 & = & \quad\text{,, lævulose} \\ & & \text{and} & & {\cdot}845 & = & \quad\text{,, cane sugar.} \end{array}$$

The percentage composition of the solid matter of the honey soluble in water is consequently

$$\begin{array}{rl} 49{\cdot}25 & \text{dextrose} \\ 41{\cdot}75 & \text{lævulose} \\ 8{\cdot}45 & \text{cane sugar.} \end{array}$$

If the sp. rot. power of a mixture of this composition be calculated, it will be found $= -9^\circ{\cdot}08$ against $-13^\circ{\cdot}4$ observed; thus:

$$\begin{array}{rcrcr} 4{\cdot}925 & \times & 5^\circ{\cdot}76 & = & 28{\cdot}36 \\ {\cdot}845 & \times & 7^\circ{\cdot}38 & = & 6{\cdot}23 \\ \hline & & & & 34{\cdot}59 \\ 4{\cdot}175 & \times & -10^\circ{\cdot}46 & = & -43{\cdot}67 \\ \hline & & & & -9{\cdot}08 \end{array}$$

There is thus a very considerable difference between the observed and calculated values, which is probably due to errors of manipulation. The analysis serves, however, to indicate the method of ascertaining the composition of a mixture of carbohydrates.

It is often necessary before a saccharine solution can be submitted to polariscopic examination to decolorize it; this may sometimes be effected by filtration through animal charcoal, but in this case the first portion of liquid which passes through is rejected, as the fresh charcoal takes up from the solution a certain amount of sugar. In the examination of molasses, which are deeply coloured, it is usual to decolorize by the addition of basic plumbic acetate; Gill, however, has shown that it is necessary to remove the excess by the addition of a strong solution of sulphurous acid before taking the observation, as the rotatory power of the *lævulose* present is modified to a considerable extent by basic plumbic acetate, even becoming reversed if a large excess of the latter be present: the effect is only temporary, and ceases with the removal of the lead. The plumbic acetate also interferes with the copper test (*Journ. Chem. Soc.*, xxiv. 91).

(1565) LACTON OR MILK SUGAR; *Lactin* or *Lactose*: $C_{12}H_{22}O_{11}$.—This carbohydrate has been found only in the milk of mammalia, being contained in greatest abundance in that of the herbivora; but it is also secreted by the carnivora, although their diet is exclusively of an animal nature. Milk sugar apparently is less subject to vary in amount than any other constituent of milk, about four per cent. being the average quantity in the milk of human females and of herbivorous animals. It may be prepared by treating milk with dilute sulphuric acid or calf's rennet to separate the albuminoid matters and the fat, then removing the coagulum, and evaporating the whey to a thin syrup; the crystals which form sooner or later are purified by several recrystallizations from water with the aid of animal charcoal. It is prepared on a considerable scale in some localities from the whey obtained in the manufacture of cheese.

Milk sugar crystallizes in hard, white, semi-transparent hemihedral rhombic prisms of the composition $C_{12}H_{22}O_{11} + OH_2$; the crystals do not give off water at 100° (212° F.), but are rendered anhydrous by heating to 130° (266° F.). The anhydrous sugar is not altered on further heating to 150°—160° (302°—320° F.), but at 170°—180° (338°—356° F.) it becomes brown, and is converted with loss of the elements of water into so-called lactocaramel; at higher temperatures it undergoes still more profound change. Crystallized milk sugar dissolves in about 6 pts. of cold, and 2½ pts. boiling water; the solution thus formed is less sweet to the taste than one containing an equal weight of cane sugar. It is insoluble in anhydrous alcohol and ether. A freshly prepared aqueous solution has a higher dextrorotatory power, in the ratio of 8 : 5, than the same solution after standing for some time or heating; the constant apparent specific rotatory power of milk sugar in solution, calculated for the anhydrous substance, according to Berthelot, is $[a]_j = 59^\circ{\cdot}3$. The influence of temperature, concentration, &c., on its rotatory power has not been studied.

Milk sugar appears to furnish a number of metallic derivatives analogous to those which may be formed from cane sugar; little, however, is known of them. It yields a precipitate with an ammoniacal solution of plumbic acetate. It does not appear to be capable of combining with sodic chloride. It is less readily acted on by acetic anhydride than cane sugar, but when boiled with it, slowly dissolves, and on pouring the product into water an almost colourless pasty mass separates, which rapidly becomes hard and brittle; this consists of the octacetate, $C_{12}H_{14}(C_2H_3O_2)_8O_3$. On evaporating the solution, an apparently crystalline residue of the tetracetate, $C_{12}H_{18}(C_2H_3O_2)_4.O_7$ is obtained (Schützenberger).

Its behaviour when heated with alkalies is similar to that of cane sugar. Concentrated sulphuric and hydrochloric acids decompose it, especially when heated, with formation of brown or black products, but much less readily than cane sugar; it is converted by a mixture of concentrated nitric and sulphuric acids into a nitrate, which crystallizes from alcohol in nacreous laminæ, and detonates when heated. Its inversion on heating with dilute sulphuric acid has already been described under lactose; it is to be remarked, however, that dilute acids and the other agents which effect the inversion act far less rapidly than on cane sugar. From Dubrunfaut's experiments (*Compt. Rend.*, xlii. 229), it appears that, as in the case of cane sugar, if the heating with dilute sulphuric acid be continued, the glucoses first produced undergo further change, a non-fermentable substance being formed, but without alteration of the rotatory power taking place. Milk sugar, like cane sugar, is not directly fermentable, but when mixed with yeast slowly undergoes inversion, yielding a mixture of fermentable glucoses; liquids, such as milk, which contain milk sugar together with nitrogenous substances and certain salts, are especially liable to undergo the lactic fermentation under the influence of *bacteria* derived from the atmosphere.

Although with most reagents it exhibits far greater stability than cane sugar, milk sugar is more easily oxidized than the latter: thus it precipitates silver from silver solutions, especially if rendered ammoniacal, the metal being deposited on the sides of the vessel so as to form a brilliant mirror if the mixture be carefully heated. In presence of an excess of alkali, it dissolves cupric hydrate, forming a deep blue coloured solution, which deposits cuprous oxide, even in the cold, but as in the case of dextrose, the amount of cupric hydrate dissolved, and the precipitation of the cuprous oxide are dependent on the amount of alkali present. Milk sugar, however, has a lower cupric oxide reducing power than dextrose in the proportion of 70 : 100; the molecular ratios in which dextrose and milk sugar reduce cupric oxide are therefore represented by the proportions $2C_6H_{12}O_6 : 10CuO$, and $2C_{12}H_{22}O_{11} : 7CuO$. By heating its aqueous solution with bromine to 100° (212° F.), and afterwards saturating the liquid with argentic hydrate, removing the dissolved silver by sulphuretted hydrogen, &c., milk sugar is converted into lactonic acid, a crystalline, optically active (lævorotatory), monobasic acid of the composition $C_6H_{10}O_6$ (Barth and Hlasiwetz, *Ann. Chem. Pharm.*, cxxii. 96). On oxidation with nitric acid, milk sugar yields mucic and saccharic acids, together with further oxidation products of these latter—viz., racemic, tartaric, and oxalic acids. It is rapidly oxidized by a boiling alkaline solution of potassic permanganate, and almost completely converted into carbonic anhydride and water; the same action takes place more slowly at ordinary temperatures, and also if the solution be strongly acid. When a neutral solution of permanganate is employed, a small quantity of a syrupy acid is formed, together with oxalic and carbonic acids (Laubenheimer, *ibid.*, clxiv. 283).

On heating milk sugar with twice its weight of aniline in an open flask, it slowly dissolves, and although no gas is evolved, the liquid froths considerably; if the product be mixed with an equal volume of alcohol and allowed to stand, crystals are deposited, and a further quantity of crystals is obtained from the filtrate after mixing it with ether. Sometimes the product consists of one, sometimes of the other, or of a mixture, of two bodies formed in accordance with the following equations:

$$2C_{12}H_{22}O_{11} + C_6H_7N = C_{30}H_{49}NO_{21} + OH_2.$$
$$C_{12}H_{22}O_{11} + C_6H_7N = C_{18}H_{27}NO_{10} + OH_2.$$

Both are very soluble in water, but very difficultly soluble in anhydrous alcohol, and almost insoluble in ether. Dextrose and mannitol also dissolve readily in aniline (Sachsse, *Deut. chem. Ges. Ber.*, iv. 834).

(1566) AMYLON OR STARCH SUGAR; *Maltose*: $C_{12}H_{22}O_{11}$.—This sugar is formed together with dextrin when starch paste is submitted to the action of diastase, or of dilute acids; its production in this manner was first demonstrated by O'Sullivan in 1872* (*Journ. Chem. Soc.*, xxv. 579; and 1876, i. 478, ii. 125), whose observations have been confirmed by Schulze (*Deut. chem. Ges. Ber.*, vii. 1047). The preparation of amylon will be described under starch.

It crystallizes from water or alcohol in hard white crusts, consisting of extremely fine needles of the composition $C_{12}H_{22}O_{11} + OH_2$; the water of crystallization may readily be expelled by drying at 100° (212° F.) in a current of dry air, or more slowly by heating to 110° (230° F.) in an air bath. It is very soluble in water, but difficultly soluble in alcohol. It is distinguished from cane and milk sugar by its superior optical activity, possessing the apparent specific rotatory power calculated for the anhydrous substance $[a]_j = +150°$. Like milk sugar, however, it is capable of precipitating cuprous oxide from Fehling's solution, but has a somewhat lower cupric oxide reducing power—viz., 65, which is in the proportion of $2C_{12}H_{22}O_{11} : 6{\cdot}5CuO$. When digested with diastase solution or with dilute sulphuric acid, it undergoes inversion, although very slowly as compared with cane sugar; the invert sugar is dextrorotatory, and has the same cupric oxide reducing power as that from cane sugar: its composition will be discussed under starch. An aqueous solution of amylon slowly ferments in contact with beer yeast, the yield of alcohol being 51—52 per cent. on the amylon taken; if a mixture of sucrodextrose and amylon be submitted to fermentation, the whole of the former disappears before the latter is touched.

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* Dubrunfaut in 1847 (*Ann. Chim. Phys.* [3], xxi. 178) isolated a body having all the properties of amylon from the product of the action of malt extract on starch, and pointed out that it was different from sucrodextrose; but his observations appear to have been long disregarded. On rediscovering this substance, and having determined its composition, &c., O'Sullivan retained the name maltose, assigned to it by Dubrunfaut, but the name amylon appears to be more suitable, both as indicating its connexion with starch, and that it is a member of the cane sugar and not of the glucose group.

(1567) MYCON; *Mycose* or *Trehalose:* $C_{12}H_{22}O_{11}$.—Wiggers in 1833 first observed this carbohydrate in ergot of rye, and it was more exactly investigated by Mitscherlich in 1857 (*Ann. Chem. Pharm.*, cvi. 15), who gave it the name of mycose (from μῦκος, fungus). Berthelot in the same year obtained a sugar from trehala-manna, which he called trehalose, regarding it as different from mycose, but was afterwards led to infer that the two were probably identical. Trehala-manna, which is used as an article of food in the East, is said to be the produce of the larvæ of a coleopterous insect (*Larinus nidificans*), which lives on a species of *Echinops;* apparently the larvæ consume the sap, but afterwards exude the greater part of the solid matter derived from it, forming with it the case in which they live, and of which the manna consists. Guibort found as much as 66·5 per cent. of starch, and 28·8 per cent. of sugar and bitter matter in the manna. Recently mycon has been shown to exist in a large number of fungi (Müntz, *Ann. Chem. Phys.* [5], viii. 56), often in considerable quantity, and more frequently together with mannitol; it is of interest that sometimes, as in the case of *Agaricus sulfureus*, for example, the younger fungi contain only mycon, whereas older specimens of the same species contain both mycon and mannitol. The more common fungi from which it may be extracted with facility are *Agaricus Eringii, sulfureus, muscarius, columbella,* and *Lactarius viridis;* it is less readily extracted from *Agaricus fusipes, lateritius, cæsareus,* and *Lycoperdon pusillum,* as they also contain mannitol; *Agaricus cornucopia, maculatus, scyphoïdes, albus, campestris* and *Cantharellus cibarius* contain only mannitol. Occasionally a fermentable sugar capable of reducing Fehling's solution is also present, being especially abundant in *Boletus externus.* Müntz was not able to detect either mycon or mannitol in yeast or *Mycoderma aceti,* but obtained mannitol from *Penicillium glaucum,* even when grown on a solution of tartaric acid, and mycon from *Mucor mucedo* and *Œthalium septicum.*

Mycon may be prepared from fungi which do not contain mannitol by precipitating the expressed juice with basic plumbic acetate, removing the excess of lead by sulphuretted hydrogen, and then evaporating to a syrup; the crystals which form are washed with cold alcohol, and purified by several crystallizations from boiling strong alcohol. Or the dried pulverized fungus is extracted with boiling alcohol, the alcoholic solution evaporated, and the residue dissolved in hot water; the crystals which separate on cooling may be purified by one or two crystallizations from alcohol. In this manner Müntz obtained 10 grams of crystallized mycon from 120 grams of dried *Agaricus Eringii*. Mycon crystallizes in shining rhombic octahedra of the composition $C_{12}H_{22}O_{11} + 2H_2O$, which may be completely dehydrated by heating to 110° (230° F.); the crystals melt if rapidly heated to 100° (212° F.), but if rendered anhydrous by gradual heating it does not melt even at 180° (356° F.), and the anhydrous substance may even be heated to 200° without undergoing decomposition, although at higher temperatures it is decomposed and converted into a black insoluble matter. It also manifests remarkable stability on treatment with reagents. Thus it may be boiled with a concentrated solution of sodic hydrate, without the liquid becoming coloured; it dissolves in concentrated sulphuric acid, forming a colourless solution, but is rapidly carbonized on heating the liquid to 100° (212° F.); and it is without appreciable action on Fehling's solution.

Mycon is extremely soluble in water, and moderately soluble in boiling, although almost insoluble in cold alcohol. It is less sweet than cane sugar. Mycon has a higher optical activity than any other sugar, its apparent specific rotatory power calculated for the anhydrous substance being $[\alpha]_j = +220°$ (Berthelot); according to Müntz, the mycon prepared from trehala-manna has the same rotatory power as that from fungi—viz., $[\alpha]_D = +200°$—the observations being made with solutions containing 5—6 per cent. of the anhydrous substance. When it is heated with dilute sulphuric acid, the rotatory power of the solution slowly diminishes until it becomes about equal to that of sucrodextrose; the nature of the invert sugar thus produced has not been ascertained, but according to Berthelot it is crystallizable, and rapidly ferments in contact with beer yeast, being completely converted into alcohol and carbonic acid, whereas mycon is scarcely altered in contact with yeast.

(1568) MELEZITON; *Melezitose:* $C_{12}H_{22}O_{11}$.—This name was assigned by Berthelot in 1856 to a sugar which he isolated from the saccharine exudation from the larch (*Pinus larix;* in French, mélèze); quite recently, however, it has also been obtained from a manna from Lahore, the produce of the *Alhagi Maurorum*, a spiny shrub of the leguminous family. This manna is used in Persia as a purgative, and even as a food material, being known by the name of *Turanjbin;* in addition to meleziton it contains cane sugar and a syrupy matter capable of reducing Fehling's solution (Villiers, *Compt. Rend.*, lxxxiv. 35).

Meleziton crystallizes in very small brilliant monoclinic prisms of the composition $C_{12}H_{22}O_{11} + OH_2$, which effloresce even at the ordinary temperature, and may be completely dehydrated by exposure over sulphuric acid in vacuo; it is about as sweet as sucrodextrose. It is extremely soluble in water, only slightly soluble in boiling ordinary alcohol, and almost insoluble in cold alcohol. The anhydrous sugar melts a little above 140° (284° F.), and decomposes when heated above 200° (392° F.). It is not decomposed by solutions of the alkalies at 100° (212° F.), and does not reduce Fehling's solution, but is carbonized by cold concentrated sulphuric acid; like mycon, it yields oxalic acid free from mucic acid when oxidised with nitric acid.

Its apparent specific rotatory power calculated for the anhydrous substance, according to Berthelot, is $[\alpha]_j = 94°.1$; according to Villiers, $[\alpha]_j = 94°.8$, and $[\alpha]_D = 88°.85$. On heating the solution with sulphuric acid, the rotatory power diminishes until it becomes equal to that of sucrodextrose; this change takes place much more slowly than with cane sugar, but more rapidly than with mycon. The glucose (or glucoses) produced is crystallizable, capable of reducing Fehling's solution, is decomposed on heating with an alkali, and readily ferments in contact with beer yeast: meleziton being only slowly altered under the influence of yeast.

(1569) Eucalypton; *Melitose*: $C_{12}H_{22}O_{11}$.—This sugar is derived from the saccharine exudation collected from various species of *Eucalyptus* growing in Tasmania; it was discovered by Johnston in 1843, and more fully examined by Berthelot in 1856* (*Ann. Chem. Phys.* [3], xlvi. 66).

It crystallizes in extremely slender interlaced needles of the composition $C_{12}H_{22}O_{11} + 3OH_2$, having a slightly sweet taste; it can only be rendered anhydrous by heating to 130° (266° F.), at which temperature, however, it already begins to decompose. Its solubility in water is about equal to that of mannitol, and like the latter it does not form syrupy solutions; a concentrated aqueous solution is not precipitated by ordinary alcohol. On oxidation with dilute nitric acid it yields a syrupy substance, which on further treatment is converted into an acid perhaps identical with mucic acid, and oxalic acid.

The specific rotatory power, calculated for the anhydrous substance, is $[\alpha]_j = 102^\circ \cdot 7$ at 25° (77° F.); on heating with dilute sulphuric acid, the rotatory power is in a few minutes reduced to $66^\circ \cdot 5$, and the inversion product has the same cupric oxide reducing power as an equal weight of eucalyptose, and is browned by alkalies, whereas eucalypton does not reduce Fehling's solution and is scarcely altered by alkalies. As already stated (1562), eucalypton also undergoes inversion when placed in contact with beer yeast, but only half the product is fermentable. Berthelot has supposed that the glucose formed together with eucalyptose on inversion of eucalypton is ordinary sucrodextrose, but the rotatory power of the fermentable glucose calculated from the values observed for the inversion product and for eucalyptose—viz., $2 \times 66^\circ \cdot 5 - 65^\circ = 68^\circ$—is considerably higher than that of sucrodextrose; Berthelot, however, expressly states that the value given for eucalyptose was deduced from a very imperfect determination.

(1570) *Saccharons artificially produced.*—Gautier has prepared a body of the same composition as cane sugar by the action of hydrochloric acid on dextrose (*Bull. Soc. Chim.* [2], xxii. 145). The carefully cooled alcoholic solution of the glucose was saturated with the gas, then heated, and evaporated over sulphuric acid in vacuo; the resulting syrup, after being neutralized with baric carbonate, was extracted with 94 per cent. alcohol, the solution evaporated in the cold, and the residue again similarly treated, and finally freed from a bitter substance by washing with ether. The body thus obtained was a colourless, extremely hygroscopic mass, easily soluble in water, resembling gum in appearance and taste, and which could only be rendered anhydrous by heating to 130° (266° F.) in a current of carbonic anhydride. It did not reduce Fehling's solution, neither was it fermentable; by heating with water at 160° (320° F.) it was decomposed in accordance with the equation $C_{12}H_{22}O_{11} + OH_2 = 2C_6H_{12}O_6$, but the product, although capable of reducing Fehling's solution, was apparently not dextro-glucose, as it had a very sweet taste and was very difficultly fermentable.

In a similar manner, by dissolving anhydrous dextrose in cold concentrated sulphuric acid, then adding alcohol and allowing the mixture to stand, Musculus (*ibid.* [2], xviii. 66) obtained a white substance having the properties of dextrin, but only about twice as great a rotatory power as dextrose.

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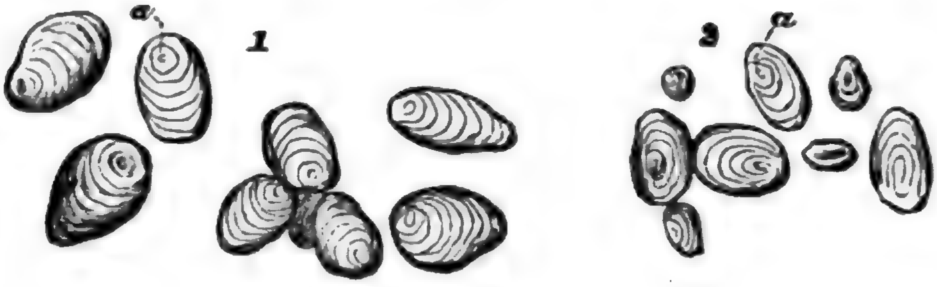
* Berthelot has termed this sugar melitose, and the glucose derived from it eucalyn (1562)—names which obviously fail to indicate the connexion which exists between the two bodies; the names eucalypton and eucalyptose indicate not only the origin of the substances which they designate, but also the relation in which they stand to each other, and the group to which each belongs.

III. CARBOHYDRATES OF THE COMPOSITION $(C_6H_{10}O_5)_n$.

(1571) STARCH ; *Amidin, Amidon, Amylum, Fecula* or *Amylaceous Matter :* $(C_6H_{10}O_5)_n$.—The great physiological importance of starch has naturally led many chemists to subject it to investigation, and far more attention has been devoted to it than to any other carbohydrate: notwithstanding this our knowledge of its behaviour long remained most imperfect and inexact, owing to the faulty nature of the methods employed, and it is only quite recently that the key to the interpretation of its nature has been discovered by O'Sullivan. His researches on the action of malt extract at various temperatures not only throw much light on the nature of starch itself, and enable us to explain the discrepant observations of previous investigators, but have in addition the great merit of indicating how such a complex problem as that involved in the determination of the nature of starch and similar carbohydrates may be successfully attacked.

Starch occurs in one or other of their organs in almost all plants with the exception of some Algæ and Lichens, and always appears in an organized form as solid grain generally having a concentrically stratified structure. These arise at first as minute masses in the protoplasm, and continue to grow while lying in it. The young small grains appear to be always spherical, but since their growth is scarcely ever uniform, their form changes into ovoid, lenticular, rounded-polyhedral, &c. They also vary greatly in magnitude in different species of plants, those from the *Canna gigantea*, for example, which affords almost the largest known, being on an average about ·175 mm. in diameter, while those from the seeds of the beetroot, which are almost the smallest known, measure only about ·004 mm.; but the grains from the same species of plant are also subject to considerable variation in size, as may readily be seen on microscopical examination of a section of potato, for example. The magnified starch grains of the Canna are represented by No. 1 of the following figures, No. 2 representing those of the arrowroot, which are similar in form and size to those of the potato; the grains of wheat starch are much smaller (about ·05 mm. in diameter), and more lenticular, while those of rice are angular. The hilum of the grain is seen at *a* in the figures.

FIG. 393.



The grains of potato starch, if illuminated by polarized light, with a Nicol's prism interposed between the object and the eye, present a well-marked black cross, the centre of which corresponds with the hilum. When wheat starch is subjected to microscopic examination in a similar manner, this cross is not perceptible; its presence may therefore be of service as a means of detecting the addition of potato starch to wheat flour.

The starch grains do not consist of the pure carbohydrate, but contain water and a very small quantity of mineral matter. The water moreover is differently distributed in the grain: most usually increasing in amount from without inwards, and attaining a maximum at a fixed point in the interior. With the increase in the proportion of water, the cohesion and density decrease, as also the index of refraction. This change in the proportion of water is not, however, constant, but intermittent. To the outermost, least watery, layer succeeds a sharply defined watery layer, to this again a less watery one, &c., until the innermost, less watery, denser layer surrounds finally a very watery part, the nucleus (Sachs). Hence it is that the grains exhibit a stratified structure. All the layers of a grain are disposed around this common centre, but every layer is not continuously developed around the whole nucleus; in small spherical grains with few layers, this is always the case, but when their number increases with growth, the number of layers increases most in the direction of most vigorous growth.

If starch from different sources be boiled for some time with water, a paste is formed which on the addition of iodine solution assumes a beautiful indigo-blue colour. The paste formed by merely warming potato starch with water sufficiently to cause the grains to swell but not to burst, is also at once coloured in this manner by iodine; but if wheat starch be similarly treated, the paste assumes only a red or bluish-violet colour according to the amount of iodine added, and it is only after heating for a relatively considerable time that the liquid is coloured a pure blue by iodine. On careful examination with the microscope of the behaviour of ungelatinized starch when placed in presence of water in contact with a crystal of previously washed iodine, it is found moreover that not only do the grains from different sources assume different shades of colour, but that different parts of the same grain become coloured with different degrees of rapidity, and even assume different shades of colour. Thus, in the case of potato starch, although the iodine must pass through the outer denser portion of the grains in order to reach the inner less dense portions, the latter become coloured first. These differences in the behaviour of starches from different sources, and of different parts of the grains, with iodine, are doubtless due to the differences in density before alluded to, and not to the existence of several distinct substances giving different colours with iodine. The coloration of starch by iodine, in fact, appears to depend not on the formation of a definite chemical compound, but to be the consequence of the mechanical interposition of the iodine between the starch molecules: according to the state of aggregation of the starch, so its attraction for iodine varies, and as the result of this, the shade of colour produced also varies, but if by continued boiling with water the state of aggregation of the various starches be equalized, they all afford the same colour—viz., blue. That starch possesses the greatest affinity for iodine in that state of aggregation in which it is coloured blue by iodine, is shown by the fact that the iodine may be withdrawn by potato starch from all substances which are coloured violet, red, or yellow.

In a similar manner the starches from different plants, and also from different parts of the grain, are acted upon and rendered soluble by maceration with saliva, malt extract, or mineral acids, with very different degrees of readiness, the starch which is coloured blue by iodine apparently being always rendered soluble most readily; thus, for example, if wheat and potato starch are together placed in the same acid, the grains of the former still exhibit a violet colour with iodine when the latter are merely coloured yellow. By more or less prolonged digestion with acids the starch grains may be almost entirely dissolved, the portions which remain exhibiting the form of the original grains of which they were the outer coatings, and apparently consist of cellulose or a closely allied substance.

Starch is the first *visible* product of the assimilation of carbonic acid by plants, but there is no evidence that it is the first product of assimilation which results from the decomposition of carbonic acid in the plant; on the contrary, there can be little doubt that its formation is preceded by that of one or more substances, of the nature of which, however, we are at present entirely ignorant. There is every reason to believe that its formation from carbonic acid takes place under the combined influence of the chlorophyll and of light, for if the young leaves of a plant be submitted to microscopical examination, the chlorophyll grains are found to be charged with starch, which gradually disappears on placing the plant in darkness; if it be then again exposed to light, the chlorophyll grains again become charged with starch, which, as before, disappears on keeping the plant in darkness. The occurrence of starch in plants destitute of chlorophyll is only an apparent exception to the above statement, as these are always parasitic on plants which contain chlorophyll; its occurrence in plants in those parts which are not only destitute of chlorophyll, but even hidden from the light, such as the tubers of the potato, for example, is in a similar manner due to the transference of the starch originally formed in the leaves to the parts in question, but how this transference takes place—*i.e.*, how the starch is rendered soluble—and in what form it is transported, is at present unknown: it has merely been ascertained that the sap in the cellular tissue which intervenes between the parts where the starch is formed and those in which it is stored up for use at a future period of growth contains a substance (? a glucose) capable of reducing Fehling's solution.

That the starch is formed more or less directly from the carbonic acid absorbed from the atmosphere has been proved by Godlewski (*Flora*, 1873, p. 383), who found that no starch is produced in the chlorophyll grains, even in the light, in an atmosphere devoid of carbonic anhydride, and that the starch contained in the chlorophyll disappears when the carbonic anhydride is removed from the surrounding atmosphere, not only in the dark, but even in bright light.

Light of all degrees of refrangibility does not equally favour the formation of starch, which proceeds vigorously in light transmitted through a solution of potassic bichromate, but only to a very limited extent in light which has passed through an ammoniacal solution of cupric sulphate; in fact, the yellow and not the violet or so-called chemical rays are most active in promoting the formation of starch. By observing the amount of oxygen evolved (which probably bears a direct relation to the amount of starch formed) in a given time on exposing a water plant, *Elodea canadensis*, in different parts of an intense solar spectrum 23 cm. long to a portion 13 mm. in breadth, Sachs has found that the different regions of the spectrum possess the following mean capacities for decomposition:

Red	25·4
Orange	63·0
Yellow	100·0
Green	37·2
Blue	22·1
Indigo	13·5
Violet	7·1

The curve representing these results coincides nearly with the curve of brightness. It is a remarkable fact that the light which is most active in promoting the evolution of oxygen from carbonic acid and water in the plant, and the formation of starch, is chiefly that which passes unabsorbed through chlorophyll.*

Lastly, it may be pointed out that certain mineral salts, notably potassium salts, are essential to the production of starch, for not only are potassium salts of constant occurrence in organs containing starch and sugar, but direct experiments have shown that starch is not formed in the absence of these salts. At present we have no conception of what their function may be; it is possible, however, that they exercise an influence similar to that which minute quantities of many acids and a number of salts exercise in the formation of condensation products and polymerides of the aldehydes (q. v.).

Starch is met with in great abundance in all dicotyledonous seeds, particularly in those of leguminous plants, such as peas and beans. The monocotyledonous seeds of the *Cerealia* or corn tribe contain it still more largely; it is also abundant in the tubers of the potato, in the roots of the *Maranta arundinacea* and *Jatropha manihot,* in the pith of the sago palm, and in many other plants. Its manufacture from one or other of these materials may now be briefly described.

Potato Starch.—The amount of starch in potato tubers differs in different varieties, and is also subject to considerable variation in the same variety, according to the conditions of cultivation; on an average they contain from 20 to 27 per cent. of starch, and from 70 to 76 per cent. of water. The cellular tissue of the tuber does not exceed 2 per cent. of the mass; in fact, there is comparatively little insoluble solid matter besides starch in potatoes, and hence the methods in use in different manufactories for extracting the starch are in principle the same, and differ only with regard to the machinery employed. The tubers are first freed as far as possible from adhering earth by a thorough washing, and are then rasped by machinery; the pulp thus obtained is received upon a sieve, and still further comminuted by means of brushes, whilst it is washed continuously by a gentle stream of water. The milky liquid which passes through the sieve is received into vats, and after the matter in suspension has subsided, the supernatant liquid is drawn off, and the deposit submitted to systematic washing with the object of separating the starch, on the one hand from the heavier earthy particles from which it is impossible completely to free the tubers by washing, and on the other from the lighter particles of cellular tissue. It is first well stirred up with water, and after a short time the milky liquid is drawn off from the deposit of sand, &c.; this milky liquid is then allowed to stand from four to six hours, during which time the heavier and larger grains of starch subside to the bottom of the vessel, while the lighter particles of cellular tissue mixed with the finer grains of starch form a layer above them. The water is now run off, the grey upper layer of the deposit carefully removed, and the residue again once or twice washed with fresh water in a similar manner; finally, it is suspended in water, the mixture run through a fine sieve, and the starch having been allowed to settle, the water is drawn off as completely as possible. It was formerly the custom to remove much of the water from the thick paste thus obtained by means of dry cloths or by placing it upon porous tiles; but the use of centrifugal machines is now becoming general for this purpose. The final drying is effected in specially constructed chambers, by the application of a moderate heat. In this way only from 66 to at most 75 per cent. of the starch present in the tubers is extracted, chiefly on account of the impossibility of effecting by mechanical means the rupture of the walls of all the cells in which it is inclosed.

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* For further information on this subject, and, in fact, for a full account of our knowledge of the manner in which starch is formed in plants, and of its physiological importance, &c., the student is referred to Sachs's "Text-Book of Botany." London: Macmillan & Co.

Wheat Starch.—Wheat contains from 50 to 75 per cent. of its weight of starch, and in addition a considerable quantity of insoluble nitrogenous matters collectively termed gluten, amounting to from 10 to 35 per cent. of its weight, the grain being usually the richer in gluten the less starch it contains. On this account starch is less readily extracted from wheat than it is from potato tubers. The oldest method, and that which is still most commonly employed, is briefly as follows:—The grain is first softened by steeping in water and is then crushed between rollers, or it is coarsely ground and then wetted with water, after which it is placed with water in a large vat, where it is allowed to remain for several days. Fermentation then takes place, chiefly at the expense of the sugar in the grain and of some of the starch, and the liquid becomes strongly acid owing to the formation of lactic and acetic acids; not only is this the case, but the gluten becomes in part dissolved by the action of the acids, and in part disaggregated, and loses its tenacity to such an extent that the starch may readily be separated from it by mechanical means, and purified by washing in the manner already described. A similar method is employed in the manufacture of starch from maize.

The starch may also be extracted by kneading the grain on a sieve with water, either after it has been ground, or after steeping it in water and then crushing it between rollers, the kneading being continued as long as the washings run through milky; the milky liquid is then allowed to ferment and become acid, so as to dissolve the gluten still adhering to the starch, the subsequent purification being effected in the usual manner by washing. The great advantage of this method is that it does not, like the previous one, involve the loss of the gluten.

Rice Starch.—In the foregoing method of preparing starch from wheat by fermentation, much of it is wasted, the whole of the gluten is lost, and the operation is attended with the continual evolution of gases of an offensive odour, which are a source of annoyance to the neighbourhood in which the manufacture is carried on. These inconveniences were overcome by Mr. O. Jones, who, in the year 1840, took out a patent for the manufacture of starch by a method which he applied particularly to rice, although it may be used with other cereal grains. Undried rice contains about 83 per cent. of starch, and about 7·0 per cent. of gluten. The process of Mr. Jones consists in separating these two materials by means of a very weak solution of alkali, which dissolves the gluten, but leaves the starch granules unaltered:—100 lb. of rice in the form of grain are macerated in five times its weight, or 50 gallons of a solution containing $\frac{1}{350}$ of its weight of caustic soda; after the lapse of 24 hours the alkaline liquid is drawn off, and replaced by water, and this having been drawn off, the rice is allowed to drain. It is next ground into a paste and passed through a fine sieve, and is then digested in fresh ley for 24 hours longer with frequent agitation. The whole is then allowed to stand for about 70 hours, when the supernatant liquid is drawn off, the deposit stirred up with water, the mixture allowed to rest for an hour, during which time the vegetable fibre subsides, and the milky liquid is then run off into a separate vessel, where the starch is deposited; finally the starch is washed, mixed with a little smalt to give it the blue tinge preferred in the market, drained, and dried in the usual manner. The liquid which floats above the starch is turbid, has a yellow colour, and contains the gluten of the grain in solution. From this liquid the gluten may be recovered by carefully neutralizing the solution with sulphuric acid.

Other Sources of Starch.—If, during the preparation of starch, the temperature employed in its desiccation be raised to 60° (140° F.), a transparent jelly is produced, which, when dry, is no longer farinaceous, but assumes the form of semi-transparent granules. *Sago* is the starch procured from the pith of the sago palm by making it into a paste with water, and pressing the mixture through a perforated metallic plate; the little cylinders thus obtained are granulated by placing them in a revolving vessel, and the granules are then exposed upon a sieve to a jet of steam, and subsequently dried. *Tapioca* is the starch of the *Jatropha manihot*, which is pressed through a colander, and dried upon a metallic plate heated to 100° (212° F.). It is thus formed into granular, semi-transparent irregular masses. *Arrowroot* is the starch of the *Maranta arundinacea*, and of one or two other tropical plants.

The starches prepared from different materials possess somewhat different properties, and one kind is often preferred to another for a given purpose: for example, it is said that rice starch is preferable to wheat starch for finishing cloth, 100 lbs. of the former being equal to 115 lbs. of the latter; and that maize starch has a greater stiffening power than either wheat or potato starch, wheat starch being superior to potato starch.

Pure starch is a white, glistening, perfectly odourless, tasteless powder. In the form in which it is usually sold, it contains about 18 per cent. of water, corresponding to the formula $C_6H_{10}O_5 + 2OH_2$, but after drying over sulphuric acid in vacuo, it has the composition $C_6H_{10}O_5 + OH_2$. It may be rendered anhydrous by heating to 100°—110° (212°—230° F.) in a current of dry air; the anhydrous substance is extremely hygroscopic. According to Flückiger, the sp. gr. of potato starch dried at 100° (212° F.) is 1·633 at 17°—18° (62°·6—64°·4 F.), but that of arrowroot starch only 1·568.

Anhydrous starch may be heated to 160° (320° F.) without undergoing change, but if heated for an hour or two at about 200° (392° F.) it becomes completely soluble in cold water. Commercial starch, on the contrary, is rendered completely soluble by heating to only 160° (320° F.) in closed vessels. The precise nature of the change which takes place is not known, but the product contains dextrin and sugar (? amylon), besides certain optically inactive substances which are without action on Fehling's solution. This soluble *torrefied* starch is known under the name of *British gum,* and is largely employed by calico printers for mixing with their colours in order to give them the requisite consistence. When starch is submitted to dry distillation, it yields carbonic anhydride and gaseous hydrocarbons, together with acetic acid and other products.

Starch is insoluble in cold water, alcohol, and ether, and does not undergo the least alteration when preserved in contact with water at ordinary temperatures; but if heated with water to a temperature which is said to vary from 45°—90° (113°—194° F.) for different varieties (comp. Lippmann, *Journ. pr. Chem.,* cxxx. 51), the grains absorb water and swell up, and finally the mixture assumes a viscous, pasty condition.

If this *starch paste* or *gelatinized* starch be largely diluted with hot water, an apparent solution of starch is obtained, from which nothing separates on cooling; it is generally considered, however, that the starch is not actually dissolved, but merely suspended in the liquid. The starch may be precipitated from the liquid by the addition of alcohol, but, according to Payen and Persoz, the form in which it separates depends on the length of time during which the starch is heated with water, the flocculi being smaller and less coherent, the longer the heating is continued. Nægeli has observed that this is also the case when the starch is separated by freezing the liquid, and then allowing it to thaw; thus, if starch be merely triturated with hot water, and the filtered liquid be then frozen, the starch separates in long, coherent threads, but if the liquid be boiled for a shorter or longer period before freezing, it is obtained in the form of short threads, irregularly-shaped flat masses or balls, being the more finely divided, the longer the heating is continued. Starch thus separated from water is coloured blue by iodine, and is without action on polarized light; it is said that after drying, it may be reduced to an extremely fine white powder, which does not form a gelatinous mass like the original starch on treatment with hot water. According to Béchamp, if starch be heated under pressure at about 150° (302° F.) with 5 to 15 times its weight of water, a limpid solution is obtained which may be readily filtered, and which as it cools deposits minute spherical granules no larger than the smallest starch grains which occur naturally. These granules are tinged blue by iodine: they are sparingly soluble in cold water, but dissolve readily when the temperature is raised to 70° (158° F.) or upwards, and hence this product is termed *soluble starch.* The aqueous solution is dextrorotatory, its apparent sp. rot. power being $[\alpha]_j = 211^\circ$; it yields a precipitate on the addition of alcohol.

Although there can thus be little doubt that starch undergoes alteration when heated with water, the nature of the alteration, and the relation which the so-called soluble starch bears to ordinary starch has yet to be ascertained.

Soluble starch is also the first product of the action of acids and malt extract on starch. Apparently it has the same empirical composition as ordinary starch, but there is not sufficient evidence to show whether it is a distinct compound, as appears probable, or merely a substance differing mechanically from the latter. Whatever its nature may be however, it appears not improbable that starch as it occurs naturally is an insoluble substance, and that the reactions manifested by a "solution" of starch are mainly those of soluble starch.

The tendency of starch to furnish metallic derivatives is far less pronounced than that of any of the carbohydrates previously considered. Ammonia does not cause starch to gelatinize, but if it be placed in contact with a 1½ or 2 per cent. solution of potassic or sodic hydrate, the granules swell up enormously, and form a tenacious paste; the tendency to absorb alkaline liquids appears to be greatly increased by drying, for if starch dried in vacuo be placed even in a 1 per cent. solution of the alkali, the granules become so distended that they burst. By precipitating the paste formed by the action of alkalies with alcohol and ether, then washing with these liquids and drying in vacuo, a product is obtained which, according to Tollens, contains for each atomic proportion of potassium or sodium from 24 to 30 atomic proportions of carbon.

A solution of starch yields precipitates on the addition of lime and baryta water, which are soluble in a large quantity of water; it also affords a white precipitate on the addition of an ammoniacal solution of plumbic acetate, which approximately has the composition $C_{12}H_{18}Pb_2O_{11}$. Tannin also affords a white precipitate with starch, which dissolves on warming the liquid, but reappears as it cools.

A solution of starch in alkali yields a blue precipitate on the addition of cupric sulphate, which is soluble in pure water and may be heated without becoming black.

According to Schützenberger, different varieties of starch are acted upon with different degrees of readiness by acetic anhydride, and the presence of more or less water in the starch also has an influence on the temperature at which the action takes place. If a mixture of anhydrous starch with 10-15 per cent. of the hydrate be heated at 140° (284° F.) with acetic anhydride, the starch swells up without dissolving, or is only partially dissolved. The product, after washing with water, is a white amorphous body, and is not coloured blue by iodine; on saponification by alkali it yields a substance which, like the original starch, is insoluble and coloured blue by iodine. When dried at 120° (248° F.), it has the composition of a triacetate, $C_6H_7(C_2H_3O_2)_3O_2$. A body of the same composition is obtained by heating anhydrous starch with acetic anhydride to about 150° (302° F.); under these circumstances the starch is dissolved, forming an amber-coloured liquid, from which water precipitates the new compound as a white amorphous substance, which is readily saponified by dilute alkalies at 100° (212° F.), yielding soluble starch. At still higher temperatures a triacetate is formed which yields dextrin on saponification; in fact, however great the excess of anhydride employed, and however high the temperature to which the mixture is heated, the triacetate is the highest derivative which can be formed.

Starch dissolves readily in cold concentrated nitric acid, and on adding water to the solution, a white precipitate of so-called *xyloïdin* is obtained, which apparently is a mono-nitrate of the formula $C_6H_9(NO_3)O_4$; if a mixture of concentrated nitric and sulphuric acids be employed, an explosive dinitrate, $C_6H_8(NO_3)_2O_3$, is produced. It is questionable whether the bodies thus obtained are directly derived from starch; Béchamp states that they differ considerably in properties according to the manner in which they are prepared, and as starch is known to undergo modification with great readiness under the influence of acids, this is by no means surprising. By reducing the mono-nitrate with ferrous chloride he obtained soluble starch.

When starch is triturated with cold concentrated sulphuric acid, a more or less coloured liquid mass is obtained, which readily dissolves in water.

Little is known of the oxidation products of starch. When it is heated with nitric acid, an abundance of oxalic acid is produced, and this acid is also formed on fusing it with potassic hydrate and a little water; it is said that in the latter case acetic and propionic acids are simultaneously produced. By heating it with water and bromine at 100° (212° F.), and subsequently neutralizing the solution with argentic hydrate, &c., it is converted into dextronic acid, $C_6H_{12}O_7$ (Habermann, *Ann. Chem. Pharm.*, clxxii. 11).

It now remains to consider the behaviour of starch in presence of dilute acids, and of the "unorganized ferments" of malt extract, saliva, &c., all of which apparently exert a similar influence, differing only in the readiness with which they induce its decomposition.

When starch paste heated to a temperature of about 60°—70° (140°—158° F.) is mixed with a cold extract of malt, the starch rapidly becomes dissolved and a limpid liquid is obtained; if a small portion of the liquid be taken at intervals, cooled, filtered, and tested with iodine, it will be found that at first it is coloured blue, but after a time reddish-brown, and finally that it ceases to yield a colour. The changes indicated by these differences in the behaviour of the solution with iodine take place somewhat rapidly if sufficient malt extract be employed; they are equally observed if the starch paste be warmed with a small quantity of sulphuric acid, and even oxalic acid may be employed to produce them, although it acts much more slowly. We are not, however, at present aware of the nature of all the changes which are thus indicated, the final stage alone having been thoroughly investigated, but we attribute the solution of the starch under the influence of the malt extract, or of the acid, to the formation of *soluble starch*—a body of which, as already stated, the relation to starch is not yet ascertained; at the time when the solution is coloured reddish-brown by iodine, it contains a substance which has received the name of *α-dextrin*, but of this we know scarcely more than of soluble starch. When the solution is no longer coloured by iodine, it contains a body capable of reducing Fehling's solution, together with a substance not having that power, the latter of which is known as *β-dextrin* or dextrin, but which in the following description will be termed *amylin*, these two substances being present in proportions which vary, as will be shown later on, according to the temperature at which the action of the malt extract has taken place. The substance capable of reducing Fehling's solution has been almost universally regarded as dextrose, notwithstanding that Dubrunfaut pointed out that its properties were altogether different from those of sucrodextrose, but as elsewhere stated, O'Sullivan has recently shown that it is a body isomeric with cane-sugar. The manner in which he has proved this, and in which *amylon*—the sugar in question (foot-note, p. 612)—and amylin are isolated from the product of the action of malt extract on starch paste may now be briefly described.

Amylon (*Maltose*).—The method employed by O'Sullivan for separating amylon from the product of the action of malt extract on starch was as follows:—100 grams of air-dried starch were mixed with 300 cc. water at 40° (104° F.), the mixture well stirred, and then poured with continual stirring into two litres of boiling water. The paste was cooled to 40° (104° F.), the cold extract from thirty grams of pale malt added to it, and the mixture kept between 40° and 45° (104° and 113° F.) for three hours. It was then boiled for some time, cooled, filtered, and the filtrate evaporated at 80° (176° F.) to 300 cc. The apparent specific rotatory power of the total solid matter in solution calculated from the sp. gr. was the same after evaporation as before boiling: hence these operations had produced no change in the substances present. The 300 cc. of syrup was boiled for a short time with two litres of alcohol of sp. gr. ·820; after cooling, the clear solution was decanted from the undissolved syrup, and put aside in a corked flask. At the end of six days the sides of the flask were covered with a crystalline crust of amylon. The substance thus obtained, after drying at 100° (212° F.), had an apparent specific rotatory power $[\alpha]_j = 150°$, and 100 pts. reduced only as much Fehling's solution as 65 parts of sucrodextrose.

Schulze and Uhrich (*Deut. chem. Ges. Ber.*, vii. 1047), instead of employing malt extract, used the diastase obtained by precipitating an aqueous extract of malt by alcohol, allowing it to act on starch paste at a temperature of about 60° (140° F.). The resulting solution was evaporated to a small bulk, and the residue mixed with alcohol; the clear liquid was then poured off from the solid matter thus separated, and evaporated to a syrup, which was boiled with strong alcohol. On cooling, the clear solution was decanted from the undissolved matter, and concentrated by evaporation over sulphuric acid; as a rule, the amylon was found to separate from this solution in the form of a syrup, which crystallized after some time. It was purified by recrystallization from water. The values obtained by Schulze and Uhrich for the apparent sp. rot. power and cupric oxide reducing power of the anhydrous substance—viz., for the former

$[\alpha]_j = 149°\cdot5$, and for the latter 66—67, agree very closely with those of O'Sullivan.

O'Sullivan appears to have placed it beyond doubt that the substance thus prepared is a definite compound, and not a mixture of a body having the same cupric oxide reducing power as sucrodextrose with a non-reducing substance; for he has found that not only can it be prepared time after time with the same properties, but also that the crystals which separate at intervals from an alcoholic solution allowed to evaporate spontaneously have always the same apparent specific rotatory power and cupric oxide reducing power, and that they may be recrystallized from water without change; he has also shown that if the product of the action of malt extract on starch be submitted to dialysis, whatever its apparent sp. rot. power, that of the solid matter in the diffusate is always $[\alpha]_j = 150°$, or thereabouts (comp. *Journ. Chem. Soc.*, 1876, i. 479).

Amylin (*β-dextrin* or *dextrin*).—The separation of this body in the pure state is much less readily effected than that of amylon, owing to the great difficulty of removing the latter from it; in fact, it has not yet been obtained perfectly free from the latter. It may be prepared by the action either of malt extract or of acids, preferably sulphuric acid, on gelatinized starch. If the former be employed, the paste, prepared as described above, from 100 grams potato starch—which is more readily acted upon than most varieties—cooled to about 70° (158° F.), is mixed with the cold extract from twenty grams of pale malt. Decomposition of the starch rapidly takes place, and after a short time it is found that a portion of the solution filtered cold is no longer coloured by iodine. When this is the case, the liquid is boiled for a short time to render the diastase inactive, then allowed to cool, and filtered from some insoluble matter which almost invariably retains the property of being coloured blue by iodine. The filtrate is evaporated on the water bath to 300 cc., and the residue mixed with alcohol of sp. gr. about ·830; this causes the separation of the amylin (dextrin) as an almost white waxy mass. In order to purify it, it is dissolved in the least possible quantity of water, and reprecipitated with alcohol; these operations being several times repeated. In order to prepare amylin by the action of sulphuric acid, the paste from 100 grams starch is heated with 10 cc. ordinary sulphuric acid until the solution, filtered cold, is no longer coloured by iodine; the acid is then removed by the careful addition of baric hydrate solution, the filtrate concentrated to 300 cc., and the syrup precipitated with alcohol.

The product thus obtained, even after it has been as often as 30 times alternately dissolved in water and precipitated with alcohol, still retains the power of reducing Fehling's solution, 100 pts. of the dry substance having the same cupric oxide reducing power as 8·5 to 9 pts. of dextrose.

The fact that the substances obtained, *a*, by the action of malt extract; *b*, by the action of sulphuric acid; and *c*, by the action of oxalic acid, exhibit the same cupric oxide reducing power, and have the same apparent sp. rot. power, viz., $[\alpha]_j = 204°—205°$ (O'Sullivan), would seem to indicate that the composition of the substance prepared by the three methods is the same, but also to suggest that the amylin has the property of reducing Fehling's solution. That pure amylin has not this property, however, there can be little doubt, as the cupric oxide reducing power may be greatly diminished if the precipitate produced by alcohol in the syrup obtained as described above from the product of the action either of malt extract or of acids on starch paste be submitted to fermentation. For this purpose it is dissolved in water, the solution boiled to drive off the alcohol, cooled to 20° (68° F.), and an amount of yeast added to it equal to about 2 per cent of the matter in solution. When fermentation is complete and the liquid has become clear, it is filtered and precipitated with alcohol; the precipitate is then dissolved in a small quantity of water, the solution filtered if necessary, and reprecipitated, this process being repeated three or four times. The supernatant liquid of the last precipitation having been decanted, the precipitate is covered with strong alcohol, which causes it gradually to break up into a white, apparently semi-crystalline, powder; this is washed two or three times with alcohol, thrown on a filter, rapidly pressed between folds of bibulous paper, and then placed over sulphuric acid. If this precaution be not quickly taken moisture is absorbed, and the powder again becomes soft and waxy. The reducing power exerted by the substance dried at 100° (212° F.) in a current of dry air, when boiled for twenty minutes with Fehling's solution, and also its apparent sp. rot. power, were determined by O'Sullivan for eight distinct preparations made in the following way:—*e*, *f*, and *g*, by the action of diastase on starch paste, stopping the transformation by boiling when the colour with iodine was no longer blue but reddish-brown; *h* and *i*, from a similar product, stopping the reaction when iodine gave no colour; *j*, by the action of sulphuric acid, the acid being separated when iodine ceased to give a blue colour, but reddish-brown; *k*, also by the action of sulphuric acid, the acid being separated when iodine gave no coloration; and *l* by the action of oxalic acid, continued until iodine gave a reddish-brown colour. The following values were obtained:

—	Apparent specific rotatory power.	Cupric oxide reducing power.
e	$[\alpha]_j$ = + 213°·0	2·03
f	+ 212°·0	2·20
g	+ 212°·7	1·24
h	+ 213°·1	1·20
i	+ 212°·7	1·40
j	+ 213°·0	1·50
k	+ 213°·5	·80
l	+ 214°·0	1·03

From these determinations there can be no doubt that the eight preparations are one and the same body. It is perhaps open to question whether the slight amount of reduction exerted by the substance thus obtained is either in part or entirely due to amylon still retained by it, but supposing the latter to be the case, and taking the average of the eight determinations, it would appear that about 2 per cent. of amylon is present; and even if the reduction be not due to amylon, there can be little doubt that amylin itself has not the power of precipitating cuprous oxide from Fehling's solution, and that it is only very slowly converted into substances which are capable of thus reducing the solution when boiled with it.

Amylin thus prepared is a brittle white powder, which exhibits no indication of crystalline structure under the microscope. When simply dried over sulphuric acid it retains 9·5 to 10 per cent. of water, corresponding to the formula $C_6H_{10}O_5 + OH_2$; it is rendered anhydrous by heating at 100° (212° F.) in a current of dry air, but the operation takes at least eight hours. It is very easily soluble in water, the solution of the anhydrous substance being attended with rise of temperature; it is not perceptibly soluble in cold alcohol of sp. gr. ·82. The aqueous solution containing 10 grams dry substance in 100 cc. at 15°·5 (60° F) has at this temperature the sp. gr. 1·03845. Its apparent sp. rot. power may be taken to be $[\alpha]_j = 213°·5$. Amylin, like starch, belongs to the class of *colloid* bodies, and does not diffuse through organised membranes.

It will be observed that to produce the preparations *c*, *f*, *g*, *j*, and *l*, the action of the diastase or acid was stopped when the colour with iodine was no longer blue, but reddish-brown, and they therefore at least partially consisted of the substance previously referred to as a-dextrin; on the other hand, the action was continued until the solution was no longer coloured by iodine in the case of preparations *h* and *k*, which therefore consisted only of so-called β-dextrin. But all the preparations have practically the same rotatory power, and as according to Béchamp the so-called soluble starch, which is coloured blue by iodine, has the apparent specific rotatory power $[a]_j = 211°$, it may be concluded that the three bodies are alike in their action on polarized light; they are also alike in composition,* so that apart from the fact that soluble starch dissolves in water only on warming, whereas the dextrins are readily dissolved in the cold, they are only to be distinguished by their behaviour with iodine.

Amylin is slowly converted into amylon when digested with malt extract, and consequently the rotatory power of the solution diminishes, whilst its cupric oxide-reducing power increases; acids produce a similar effect. Amylon itself also undergoes change when submitted to the prolonged action of diastase, or of sulphuric acid, but the change takes place with extreme slowness, especially if diastase be the agent; the nature of the glucose, or glucoses, into which amylon is thus converted will be discussed later on.

We have now to consider the action of malt extract on starch paste at different temperatures, for O'Sullivan has established the remarkable fact that although, if the action be stopped when the solution is no longer coloured by iodine, the product is always a mixture of amylon (maltose) and amylin (dextrin), the proportions in which the two bodies are obtained varies with the temperature (*Journ. Chem. Soc.*, 1876, ii. 125).

There can be no doubt that amylon and amylin are the only products of the transformation of starch under the influence of malt extract, if the action be stopped when iodine no longer colours the solution; for if the amount of solid matter present be determined (foot note, p. 597), and its composition be calculated on this supposition, the amount of amylon it contains being deduced from its cupric oxide-reducing power,† and the amount of amylin by deducting the amount of amylon thus found, and the rotatory power of the mixture be then calculated, the sp. rot. powers of the two bodies being taken as $[a]_j = 150°$ and $213{\cdot}5°$ respectively,‡ the value thus obtained closely agrees with that directly observed. The same is true of the residue obtained on extracting the crude product of the action of diastaste on starch paste with alcohol. The following are examples of results obtained in this manner by O'Sullivan:

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* O'Sullivan found 44·16 per cent. carbon and 6·44 per cent. hydrogen in a sample of a-dextrin, and 44·23 per cent. carbon and 6·36 per cent. hydrogen in a sample of β-dextrin, the theoretical numbers being 44·44 and 6·17. The slight excess of hydrogen and deficiency of carbon exhibited by these analyses is doubtless due to the presence of at least 2 per cent. of amylon in the substances analysed.

† Since 100 parts amylon have the same reducing power as 65 parts dextrose, the amount of amylon is calculated by dividing the number which expresses the cupric oxide-reducing power by ·65.

‡ From the definition of sp. rot. power given on p. 572, it will be evident that the amount of rotation produced by 1 gram of active substance in 100 cc. of solution will be $\frac{1}{10}$th of the apparent sp. rot. power of the substance in a solution of the concentration employed; therefore, in order to calculate the rotatory power of a mixture of amylon and amylin, the number of grams of each in 10 grams of mixture must be multiplied by 15° and 21°·35 respectively, and the two products added together. Thus, to find the apparent sp. rot. power of a mixture containing 6·77 grams amylon and 3·23 grams amylin, we have $(6{\cdot}77 \times 15°) + (3{\cdot}23 \times 21°{\cdot}35) = 170°{\cdot}5$.

Cupric oxide reducing power.	Amylon.	Amylin.	Calculated apparent sp. rot. power.	Observed apparent sp. rot. power.
44	67·7	32·3	170°·5	170°·8
16	24·6	75·4	197°·9	197°·5
9	13·8	86·2	204°·7	204°·6
8	12·3	87·7	205°·7	205°·5
10	15·3	84·7	203°·8	203°·7

Cold malt extract is entirely without action on ungelatinized starch, but begins to dissolve it at the temperature of gelatinization or a few degrees lower. Starches from different sources, however, and even the granules of the same sample, are not all attacked at the same temperature. Thus, if malt extract be added to the starch, and the temperature gradually raised, a certain portion is dissolved at one point, and a further portion at a higher temperature, and so on. The complete solution of potato starch is only effected at 62°–64° (143°·6–147°·2 F.); maize, rice, and the small granule starches in general, require a temperature many degrees higher; in some cases the transforming power of the diastase is destroyed before some of the granules become gelatinized. On this account, the complete solution of some of the starches cannot be effected; rarely, however, does the quantity remaining insoluble exceed 4 per cent.

Malt extract dissolves gelatinized starch at a temperature of 10°–20° (50°–68° F.) almost completely if the gelatinization be perfect. From a large number of experiments, O'Sullivan finds that if the solution be filtered and analysed within a few hours of adding the extract to the paste, amylon and amylin are formed in the proportion of about 67 per cent. of the former to 33 per cent. of the latter; but if the reaction be allowed to extend over a greater length of time, the amylon increases at the expense of the amylin, especially if the converting agent be in excess, as much as 90 per cent. of amylon being sometimes obtained.

If the transformation take place at a higher temperature, *not exceeding* 63° (145°·4 F.), the product also invariably contains amylon and amylin in proportion closely agreeing with those required on the assumption that the starch is decomposed in the manner represented by the following empirical equation:

$$\text{(A.)}\quad \underset{\text{Starch.}}{(C_6H_{10}O_5)_{12}} + 4OH_2 = \underset{\text{Amylon.}}{4C_{12}H_{22}O_{11}} + \underset{\text{Amylin.}}{2C_{12}H_{20}O_{10}}.$$

A mixture of amylon and amylin in the proportions indicated by this equation should consist of 67·85 per cent. of amylon and 32·15 per cent. of amylin, and should exhibit the apparent sp. rot. power $[\alpha]_j = 170^\circ{\cdot}4$; the following are the results obtained by O'Sullivan in four experiments made respectively at 30° (86° F.), 40° (104° F.), 50° (122° F.), and 60° (140° F.):

Percentage of Amylon.	Percentage of Amylin.	Observed apparent sp. rot. power.	Calculated apparent sp. rot. power.
68·1	31·9	169°·7	170°·2
67·4	32·6	170°·7	170°·7
66·7	33·3	169°·9	171°·1
68·3	31·7	170°·8	170°·1

If, however, starch paste be decomposed by malt extract at any temperature between 64° and 68°—70° (147°·2 and 154°·4—158° F.), a relatively smaller amount of amylon is obtained than at lower temperatures, amylon and amylin being formed in proportions closely agreeing with the equation:

$$\text{(B.)}\quad \underset{\text{Starch.}}{(C_6H_{10}O_5)_{18}} + 2OH_2 = \underset{\text{Amylon.}}{2C_{12}H_{22}O_{11}} + \underset{\text{Amylin.}}{4C_{12}H_{20}O_{10}}.$$

And at still higher temperatures, viz., at temperatures from 68°—70° (154°·4—158° F.) to the point at which the activity of the diastase is destroyed, even a still smaller proportion of amylon is obtained, the transformation which then takes place being indicated by the equation:

$$\text{(C.)}\quad \underset{\text{Starch.}}{(C_6H_{10}O_5)_{12}} + OH_2 = \underset{\text{Amylon.}}{C_{12}H_{22}O_{11}} + \underset{\text{Amylin.}}{5C_{12}H_{20}O_{10}}.$$

The formation of amylon and amylin in these various proportions at the temperatures specified is observed only when the starch paste and malt extract are separately heated to the particular temperature, care being taken that the latter is not heated to a higher temperature, and are then mixed; very different results are obtained if the malt extract be heated to a higher temperature than than that at which the reaction is allowed to take place previous to mixing it with the starch paste. Thus O'Sullivan has found that if starch paste cooled to 60° (140° F.) be mixed with malt extract heated to 67° (152°·6 F.) for a few minutes and then cooled to 60° (140° F.), decomposition does not ensue in accordance with the equation A above given, but as represented by the second equation (B); and that, similarly, if the malt extract be heated to 75° (167° F.), then cooled to 68° (154°·4 F.), and allowed to act on starch paste at this latter temperature, the transformation takes place in accordance with equation C. It would therefore seem that the remarkable difference in the results obtained at different temperatures is due to some change brought about by heat in the character of the decomposing agent or agents in the malt extract.

It has already been pointed out that the transference of starch in plants from one part to another must be preceded by its conversion into a soluble form; but not only must the product be soluble, it must also be capable of passing through the cell walls. It is highly probable that the change which the starch undergoes is similar to that which takes place when it is submitted to the action of diastase, and that it is converted into amylon and amylin, the latter being also subsequently converted into amylon, but much more slowly. In this connexion it is an interesting fact that the greatest relative proportion of amylon is produced when starch is decomposed at low temperatures; hence, as amylon is readily diffusible, whereas amylin is a colloid substance, the conditions are such as most to favour the rapid transference of the starch.

The proportions of amylon and amylin above given as constituting the product of decomposition at the various specified temperatures are those which are obtained when the malt extract and starch paste, both heated to the temperature at which it is desired the reaction shall take place, are mixed and the mixture placed on a water bath heated to a like temperature, the solution being removed from the water bath as soon as the starch paste dissolves, rapidly cooled and filtered from a small amount of insoluble matter. If sufficient malt extract be employed, the solution of the starch is completed within a very few minutes, the insoluble matter which remains seldom amounting to ·5 per cent. of the air-dried starch employed, and the filtrate giving no colouration with iodine, although if the solution be heated immediately to the boiling point before removing the insoluble matter the filtrate almost always gives a blue or reddish-brown colour with iodine. But unless the malt extract employed be in considerable excess, very little change takes place in the proportions of amylon and amylin at first produced, even if the solution be maintained for four or five hours at the temperature at which the decomposition is effected; if, however, the malt extract be in excess, or strongly acid, the amylin slowly undergoes conversion into amylon, and if the unboiled solution be digested for a sufficient time, the greater part of the amylin may be transformed into amylon, so that by varying the time of digestion and the quantity of the transforming agent any proportions of amylon and amylin may be obtained: hence the discrepant statements of previous observers, 'as to the relative proportions of dextrin and "sugar" produced by the action of malt extract on starch under various conditions.' If the solution be boiled previous to digestion, the amylin is not converted into amylon to any extent, the transforming agent in the malt extract being thereby rendered inert.

The quantity of malt extract required to effect the transformation of starch into amylon and amylin can only be approximately determined, as the cold extracts of different malts exhibit very different transforming powers; a quantity of extract containing solid matter equal to 5 per cent. of the starch taken, is sufficient, however, in almost all cases.

If the digestion with an excess of malt extract be continued for several hours, especially if the extract contain more acid than usual, it is found that the rotatory power of the product, calculated from its cupric oxide reducing power, &c., (p. 630), is invariably greater than that directly observed, in consequence of the partial conversion of the amylon into glucoses having a lower rotatory power. This conversion of amylon into glucoses under the influence of malt extract, which takes place very slowly, is regarded by O'Sullivan as an effect produced, not by a special transforming agent, but by the acid it contains; this conclusion is supported by Schulze and Uhrich's observation that amylon is not altered when digested with "diastase" prepared by precipitating malt extract with alcohol.

It is generally supposed that the glucose into which starch is finally converted by digestion with dilute sulphuric acid is ordinary dextrose, inasmuch as the product has the same cupric oxide reducing power as sucrodextrose, which it resembles in other respects. O'Sullivan's experiments, however, appear to indicate that amylon is converted into two dextrorotatory glucoses on inversion, one of which at least is different from sucrodextrose. Thus he found that on digesting 10 grams pure amylon with malt extract containing ·7 gram solid matter for ten hours, the cupric oxide reducing-power increased to 73, while the apparent sp. rot. power fell to $[\alpha]_j = +131°$. From these numbers the amount of glucoses produced, and their combined apparent sp. rot. power, may be calculated in the following manner, bearing in mind that the cupric oxide reducing power of amylon is 65, while that of the glucoses produced by its inversion is 100.

$$\begin{aligned} \text{Let } x &= \text{the amount of amylon remaining unchanged} \\ \therefore\ 10 - x &= \text{the amount of glucoses produced} \\ \text{then } x \times {\cdot}65 + 10 - x &= 7{\cdot}3 \\ {\cdot}35\,x &= 2{\cdot}7 \\ \therefore\ x &= 7{\cdot}71 \\ \text{and } 10 - 7{\cdot}71 &= 2{\cdot}29\text{, the amount of glucoses produced.} \end{aligned}$$

Then $131° - (7{\cdot}71 \times 15°) = 15°{\cdot}35$, the activity of 2·29 grams of the glucoses in 100 cc. of solution; hence $\frac{15{\cdot}35}{2{\cdot}29} = 6°{\cdot}7$ is the activity of 1 gram, and therefore the apparent sp. rot. power = 67. In like manner, in a number of experiments on the inversion of amylon by dilute sulphuric acid, it was found that when the apparent sp. rot. power reached 67° the cupric oxide reducing power was always 100 (*private communication*).

'O'Sullivan is inclined to regard the product of the inversion of amylon as a mixture of two dextroglucoses, both different from sucrodextrose; the observations of Tollens (*Deut. chem. Ges. Ber.*, ix. 487, 1531), however, on the optical behaviour of the glucose from starch do not favour this conclusion. This chemist has carefully examined the influence of concentration on the apparent sp. rot. power of dextrose, employing for most of his experiments so-called pure commercial grape sugar. This had been prepared from the best commercial "grape sugar" (from starch) by dissolving it in alcohol and precipitating with ether; but in order further to purify it, Tollens recrystallized it twice from water, then once from 80 per cent. alcohol, and again once or twice from water. The apparent sp. rot. power of the substance thus obtained was found to be the same as that of sucrodextrose in a solution of the same strength,* and was not altered by recrystallization; hence it may be concluded that amylon yields sucrodextrose on inversion.

Admitting this to be the case, it may be calculated from O'Sullivan's determination of the apparent sp. rot. power of the mixture of glucoses from amylon that the apparent sp. rot. power of the glucose which accompanies sucrodextrose is $[\alpha]_j = 67^\circ \times 2 - 57^\circ\cdot6 = 76^\circ\cdot4$.

It is certainly remarkable, however, if amylon yields sucrodextrose and a dextrose of considerably higher rotatory power on inversion, that the former should be so readily and completely separated from the latter by mere crystallization from water and alcohol as would appear to be the case from Tollens' observations; in fact, although there can be little doubt that the final product of the action of acids on starch is not merely sucrodextrose, as has been very generally supposed, it must be admitted that at present there is not sufficient evidence as to what is exactly the nature of the product.

Action of Acids on Starch at Ordinary Temperatures.—Starch slowly undergoes alteration when allowed to remain at ordinary atmospheric temperatures in contact with hydrochloric or sulphuric acid of such strength as not to cause the granules to swell, being acted upon the more rapidly, the more concentrated the acid.

According to Nægeli,† if potato starch and a 12 per cent. solution of hydrochloric acid, or a 15–16 per cent. solution of sulphuric acid, in the proportion of 1000 grams air dried starch to 6 litres of acid, be placed in a stoppered bottle, and the mixture shaken daily, very little alteration of the starch is apparent; the liquid gradually assumes a pale yellow tint, and the granules become less coherent, but they do not alter in bulk; and if submitted to microscopic examination, they exhibit no alteration of either form or structure, excepting that the stratification appears more marked. But when tested as to their behaviour with iodine, whereas at first they are coloured blue, after about twelve days they assume a violet colour, then a red colour, and finally, after about three weeks, are coloured

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* According to Tollens' observations, the apparent specific rotatory power of dextrose (from starch) in aqueous solution increases with the concentration; for solutions containing a given number of grams of hydrated dextrose, $C_6H_{12}O_6 + OH_2$, in 100 grams it may be calculated by the aid of the following formula:

$$[\alpha]_D = 47^\circ\cdot92541 + 0\cdot015534\,P + 0\cdot0003883\,P^2.$$

Hence the sp. rot. power of the pure hydrate is $53^\circ\cdot36$, and that of the anhydrous substance $58^\circ\cdot70$; the value $47^\circ\cdot92541$ is that calculated for $P = 0$ or q (p. 575) = 100.

† *Beiträge zur näheren Kenntniss der Stärkegruppe. Leipzig: W. Engelman.* 1874. In this pamphlet (115 pp. oct.) Nægeli not only describes his own observations, but also gives a brief analysis of the various investigations on starch previously published.

reddish-yellow. The changes indicated by these differences of colour do not take place precisely at the same time in all the granules; after a time, however, a point is reached when all exhibit a yellow colour with iodine, and from this time on, iodine fails to indicate any further change.

Nægeli ascertained the rate at which the starch is altered and dissolved, by weighing at intervals the residue dried at 100° (212° F.). He found that after thirty-six days, when most of the granules were coloured yellow or reddish-yellow by iodine, and only a few assumed a faint violet tinge, 100 parts of anhydrous starch had lost 38·5 parts; after 115 days, when all the granules were uniformly coloured yellow by iodine, 100 parts of anhydrous starch had become reduced to 29·5 parts; after 240 days only 17·2 parts remained undissolved; but even after 720 days there was a residue equal to about 6 per cent. of the starch taken, consisting of mere skeletons of the granules. The solution of starch under the influence of acids at ordinary temperatures apparently, therefore, takes place more slowly the longer the digestion is continued; this is probably due, at least in part, to the inhibiting action of the products in solution, as the starch was found to be much more rapidly dissolved if the acid were renewed at intervals.

The residual matter obtained when starch is allowed to remain in contact with hydrochloric acid until the granules are uniformly coloured yellow by iodine is no longer starch, however,* for according to Nægeli, if it be entirely freed from acid by washing with water (by decantation) and then boiled with water, by far the greater part dissolves; and if the solution be filtered and then frozen, on thawing the frozen mass, a turbid liquid is obtained, from which after a time a snow-white deposit separates, whilst the supernatant liquid is perfectly clear. Under the microscope this deposit is seen to consist of disc-shaped masses, which apparently possess crystalline structure, as when viewed by polarized light they exhibit a black cross, and if a plate of selenite be interposed between the Nicols, the different parts of the discs appear differently coloured. Nægeli has termed this substance *amylodextrin;* it is probably identical with the substance previously termed *a*-dextrin. Its properties are as follows. It is not soluble in cold water, but readily dissolves on heating to 60°—65° (140°—149° F.); it does not separate from the solution on cooling, but if the solution be evaporated to a thick syrup, although nothing separates at first, after a time the whole solidifies to a mass of the discs. It is precipitated from its aqueous solution by alcohol, but does not yield a precipitate with baric hydrate, ammoniacal plumbic acetate, or tannin. When placed in contact with water and a crystal of iodine, it is either not coloured at all, or assumes only a faint yellowish-red tinge, but if a crystal of iodine be added to its solution the liquid becomes at first violet, then reddish-violet, and finally purple-red. Nægeli supposes it to be without action on Fehling's solution, although he found that 100 pts. of the substance dried over sulphuric acid reduced as much of the solution as 6·85 pts. dextrose, but he attributes this to its conversion into sugar by the action of the alkali, as it had a much greater reducing power after heating for a short time with a weak solution of potassic hydrate; probably, however, his amylodextrin contained amylon. It is remarkable that amylodextrin, dried over sulphuric acid, lost only 1·75 per cent. water at 100° (212° F.), as according to O'Sullivan, when *a*-dextrin is dried over sulphuric acid its weight becomes constant when it contains 9·5 to 10 per cent. water.

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* The assumption has been made that the substance coloured yellow by iodine is pre-existent in starch—that potato starch, for example, chiefly consists of the modification coloured blue, and of that coloured yellow by iodine, the former of which is more readily extracted by acids, and is therefore first removed. There is, however, no evidence to warrant this.

The results obtained by Nægeli appear to indicate that acids exercise precisely the same action on starch at ordinary atmospheric temperatures as at higher temperatures, the only difference being that alteration takes place much more rapidly in the latter case; they are more particularly of interest in connexion with the formation of α-dextrin (amylodextrin), and indicate the method by which probably it will be possible to obtain it in a state of purity; but they do not afford any evidence as to whether it is produced alone, or together with amylon, which is the most important point to decide.

The products which appear to be successively formed from starch by the action of malt extract (and probably also of saliva, pancreatic juice, and other similar substances), or of acids, are therefore as follows:

1. *Soluble starch* $(C_6H_{10}O_5)_n$	Probably formed alone. Is coloured blue by iodine; does not dissolve in cold water, but readily on heating; may be separated from the solution by freezing.
2. *α-Dextrin* (*amylodextrin*) $(C_6H_{10}O_5)_n$	Whether formed alone, or together with amylon, uncertain; not dissolved by cold water, but immediately on heating to 60°–65° C.; may be separated from the solution by freezing, in characteristic disc-shaped masses; the solution is coloured reddish-brown by iodine.
3. *Amylin* (*β-dextrin*) $(C_{12}H_{20}O_{10})_n$ and *amylon* $C_{12}H_{22}O_{11}$	Formed simultaneously in proportions varying with the temperature, if malt extract be employed. Amylin dissolves readily in cold water, and cannot be separated except by the addition of alcohol to a very concentrated solution; the solution is not coloured by iodine.* The three bodies, soluble starch, α- and β-dextrin, have probably the same apparent sp. rot. power in solution—viz., $[\alpha]_j = 213°$ (about), and are not diffusible through organised membranes.
4. *Amylon* (*maltose*) $C_{12}H_{22}O_{11}$	Gradually formed from the amylin, and probably when malt extract is employed by the action of the diastase and not of the acid it contains. A crystalline substance, very soluble in water; readily diffusible; cupric-oxide reducing power = 65; apparent sp. rot. power in solution $[\alpha]_j = 150°$.
5. *Two Dextroglucoses* $C_6H_{12}O_6$	The mixture has the same cupric oxide-reducing power as sucrodextrose, but an apparent sp. rot. power $[\alpha]_j = 67°$; is perhaps a mixture of sucrodextrose and a dextroglucose of the apparent sp. rot. power $[\alpha]_j = 76°\cdot4$. Their formation from amylon by the action of malt extract is probably due to the acid it contains; even sulphuric acid, however, only slowly causes the inversion of amylon.

(1572) PARAMYLON.—According to Gottlieb (*Ann. Chem. Pharm.*, lxxv. 51), the cells of a species of alga, the *Euglena viridis*, contain a large

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[*] Nægeli states that although a solution of dextrin is scarcely coloured by a weak solution of iodine, if a crystal of the latter be added it assumes a reddish-brown colour.

number of small granules consisting of a substance of the same composition as starch, and closely resembling it in appearance, but not coloured by iodine. It may be extracted by first thoroughly exhausting the *Euglena* with alcohol and ether to separate colouring matter, &c., and then macerating it at the ordinary temperature with a dilute solution of potassic hydrate; on acidulating the solution, it is thrown down as a transparent gelatinous precipitate, which, when dry, forms a gum-like mass. Paramylon, as this substance has been termed, is not soluble in water, and is not altered by boiling with dilute hydrochloric acid, but the concentrated acid rapidly converts it into a body capable of reducing Fehling's solution, and yielding alcohol on fermentation. According to Habermann, by heating it with water and bromine, and subsequently neutralising with argentic hydrate, &c., an acid is obtained very similar to that from starch (p. 626).

(1573) SYNANTHROSE: (?) $C_{12}H_{20}O_{10} + OH_2$.—This carbohydrate accompanies inulin in all the tuber-bearing *Compositæ* or *Synanthereæ*, being most abundant in the ripe tubers; it was first described by Popp in 1870 (*Ann. Chem. Pharm.*, clvi. 181). The best materials for its preparation are the tubers of *Dahlia variabilis* or of the Jerusalem artichoke (*Helianthus tuberosus*). The expressed juice of the freshly-gathered tubers is precipitated with basic plumbic acetate, the dissolved lead removed by sulphuretted hydrogen, the solution neutralized with magnesic carbonate, and evaporated on the water bath. The residue is then repeatedly extracted with small quantities of alcohol, until it is deprived of optically active substances; after drying the undissolved portion on the water bath, in order to free it from water and inulin, it is fractionally treated with small quantities of aqueous alcohol, so as to obtain as saturated a solution as possible. This solution, after being completely decolorized by animal charcoal, is poured in a thin stream into a mixture of ether and anhydrous alcohol; the precipitate is then quickly filtered off, washed with ether-alcohol, and dried over sulphuric acid in vacuo. It is thus obtained as a white, incoherent, bulky, amorphous mass of the composition $C_{12}H_{22}O_{11}$; it is extremely hygroscopic and deliquescent, easily soluble in water and aqueous alcohol, difficultly soluble in absolute alcohol, and insoluble in ether. It has an insipid taste, without being in the least sweet. The substance which has been in contact with water retains a molecule of water with great persistency, and cannot be rendered anhydrous by mere drying in the air bath without suffering decomposition; it appears also to possess a similar affinity for alcohol. It is not only optically inactive, but also without immediate action on Fehling's solution, although the latter is reduced after long boiling, owing to the alteration of the synanthrose by the alkali; it immediately causes the precipitation of mercury from a solution of mercurous nitrate. After heating synanthrose with dilute acids, however, the solution has a powerful lævorotatory action, in consequence, according to Popp, of the conversion of the synanthrose into a mixture of dextrose and lævulose; but he does not mention on what evidence this conclusion is based, and his statement that the apparent specific rotatory power of the inversion product ($[\alpha]_j = -54{\cdot}09$ at 17° (62°·6 F.) in a solution containing about 2 per cent.) is not appreciably modified by an alteration of temperature, is opposed to this conclusion, as the rotatory power of sucrolævulose is known to vary very considerably with the temperature. Moreover, the behaviour of synanthrose in presence of beer yeast is remarkable: although not directly fermentable, it appears to undergo inversion under the influence of the yeast, and to furnish fermentable products, but according to Dieck and Tollens (*Journ. f. Landwirthschaft*, xxiv. 117) the fermentation takes place very slowly, and only about two-thirds as much gas is evolved as would be obtained from an equal weight of dextrose.

On heating synanthrose to 140°—145° (284°—293° F.), it becomes brown and gas is evolved, apparently undergoing a change similar to that which takes place when cane sugar is carefully heated; on submitting it to dry distillation, gases are evolved, and a distillate obtained containing acetic acid and acetone. On oxidation with dilute nitric acid, it yields saccharic and oxalic acids. Its aqueous solution is not precipitated by normal or basic plumbic acetate, but a lead derivative may be obtained by precipitating an alcoholic solution with an alcoholic solution of the basic acetate; and calcium and barium derivatives are precipitated on the addition of alcohol to solutions of synanthrose in lime or baryta water. It is not browned by a cold solution of potassic hydrate, and although blackened by concentrated sulphuric acid, it is not so much acted on as cane sugar.

(1574) INULIN : $(C_6H_{10}O_5)_n$.—This carbohydrate replaces starch in the root system of many *Compositæ*, being especially abundant in the tubers of the dahlia (*Dahlia variabilis*), which when ripe contain as much as 10 per cent. of their weight of inulin, and of the Jerusalem artichoke (*Helianthus tuberosus*), and in the roots of elecampane (*Inula Helenium*), dandelion (*Taraxacum officinale*), and chicory (*Chicorium Intybus*),

According to Kraus (*Bot. Zeitg.* 1875, 171), it is not confined to the biennial and perennial compositæ, as supposed by Dragendorff,* but is also found in the *Campanulaceæ*, *Goodeniaceæ*, *Lobeliaceæ*, and *Stylideæ*; and occurs abundantly in these plants, not only in the underground organs, in which alone it is found in the *Compositæ*, according to Dragendorff, but also in the fleshy stems of the *Cacaliæ* and *Kleiniæ*, in the woody stem of *Musschia*, in the herbaceous stalks of *Stylidium suffructicosum*, and in the green creeping stalk of *Selliera radicans*, and even occurs in the chlorophyll cells of the fleshy leaves of these plants. The inulins of different plants, however, are not all equally soluble in water, according to Kraus. In the *Compositæ*, at least, inulin apparently has a similar function to that which starch exercises in potato tubers, for example, being stored up during the earlier period of the plant's growth for use at a future period of growth, and is generally most abundant in the autumn.

Preparation.—It is difficult to prepare pure inulin, as it is usually accompanied by gummy and albuminous matters, and also has a great tendency to retain various salts. It is most readily obtained in a pure state from dahlia tubers in autumn. The well-washed tubers are reduced to a fine pulp, which is rapidly pressed, and the expressed liquid is allowed to stand 12—18 hours, after which it is mixed with at most an equal volume of alcohol, the precipitate, consisting chiefly of impurities, is rapidly filtered off, and the inulin then separated by the addition of double the quantity of alcohol. It may be further purified by dissolving it in hot water and again fractionally precipitating with alcohol.

Another method of obtaining inulin is to digest the substance containing it with water heated to about 90° (194° F.); the extract thus obtained is treated with basic plumbic acetate, which precipitates most of the impurities, the precipitate removed by filtration, the dissolved lead thrown down by sulphuretted hydrogen, the filtrate from the plumbic sulphide neutralized with ammonia and then concentrated on the water bath, and finally the inulin precipitated with alcohol. In order to prevent caking, the inulin thus prepared must be at first dried at a low temperature, not exceeding 50° (122° F.).

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* *Materialien zu einer Monographie des Inulins, St. Petersburg : H. Schnitzdorff*, 1870.—This monograph contains a critical analysis of all previous investigations of inulin, and also an account of a considerable number of original experiments.

Pure inulin is a brilliant white powder, resembling starch in appearance, but readily distinguished from the latter, as it dissolves in warm water, forming a perfectly clear and limpid solution, which is not coloured by iodine; if it be very slowly separated from its aqueous solution by alcohol, it forms globular aggregates presumably of needle-shaped crystals—so-called sphœro-crystals, which exhibit under the polarizing microscope a black cross similar to that displayed by the granules of potato-starch. (Comp. Sachs' *Text Book of Botany*, 1875, p. 63).* It is scarcely dissolved by cold water, although according to Sachs and Dragendorff, it readily dissolves in water heated to about 55° (131° F.); Prantl states, however, that whereas 100 cc. of a solution saturated at 0° (32° F.) contain only ·01 gram inulin, 100 cc. of a solution saturated at 100° (212° F.) contain no less than 36·50 grams; and that solutions saturated at 14° (57°·2 F.), 30° (86° F.), 60° (140° F.), and 80° (176° F.) contain in 100 cc. respectively ·2, ·27, 1·57 and 4·0 grams of inulin. The inulin is not entirely deposited as the solution cools; indeed a solution containing 4 or 5 per cent. often remains clear for days if protected from dust, but on cooling it strongly, or adding alcohol or glycerin, the inulin is at once precipitated.

This behaviour affords an explanation of the occurrence of such relatively large amounts of inulin in solution in the cell sap of the *Compositæ*, and its slow separation from the expressed juice. Dragendorff has found that when solutions containing from 2 to 12 per cent. of inulin are allowed to diffuse through parchment paper into water, the diffusate never contains more inulin than water of the same temperature dissolves when in contact with the solid substance. He also states that if a solution prepared by dissolving inulin in warm water be evaporated either at the ordinary temperature in vacuo, or in the water bath, the precaution being taken to exclude dust by stopping the mouth of the flask with cotton wool, an amorphous residue is obtained which dissolves much more readily in water than ordinary granular inulin, which very soon, however, begins to separate from the solution thus obtained. He therefore assumes that inulin exists in two modifications, one of which is crystalline and difficultly soluble, and the other amorphous and easily soluble, and that the former is converted into the latter by heating with water to about 55° (131° F.), whilst the latter is reconverted into the former by contact with dust, and by the dehydrating action of substances such as alcohol, glycerin, &c. It appears more probable, however, that by heating with water the inulin acquires a greater attraction for water, and perhaps enters into combination with it to form a more soluble hydrate.

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* The presence of inulin in plants may be demonstrated by placing thin sections first for a few minutes in 90 per cent. alcohol, and then for a short time in water, after which they are submitted to microscopic examination. If sphœro-crystals are observed, it is not only necessary to examine their behaviour with polarised light, but also to ascertain that they are readily dissolved on warming with water to about 50°—55° C., and also on treatment with potassic hydrate solution and dilute nitric and hydrochloric acids. The solution of the inulin crystals by these reagents always commences from without.

Air-dried inulin has the composition $C_6H_{10}O_5 + OH_2$, and may be rendered anhydrous by heating to 100° (212° F.); the anhydrous substance has the sp. gr. 1·470, whilst a solution containing 10 per cent. of inulin has the sp. gr. (?) 1·0396 at 20° (68° F.) (Dragendorff). According to Dubrunfaut, anhydrous inulin is not altered when heated to 180° (356° F.), but melts and undergoes decomposition at higher temperatures; Dragendorff, however, states that it melts at 165° (329° F.), but without suffering decomposition.

An aqueous solution of inulin exerts a lævorotatory action on polarized light; the apparent sp. rot. power of inulin has not, however, been satisfactorily determined.

Bouchardat (1847) gave the value $[\alpha]_r = -26^{\circ}{\cdot}16$, but did not state whether this applies to the anhydrous substance; Dubrunfaut (1856) found $[\alpha]_j = -44^{\circ}{\cdot}9$ and $[\alpha]_r = -34^{\circ}{\cdot}2$; and Dragendorff (1870) states that in a solution containing about 5 per cent. of dahlia inulin $[\alpha]_D = -34^{\circ}{\cdot}42$ at 20° (68° F.), these values being calculated for the anhydrous substance; according to Schützenberger, however (*Ann. Chem. Pharm.*, clx. 82), who appears to have used a Wild's polaristrobometer and ordinary white light, dahlia inulin has the apparent sp. rot. power −26°, whereas that of elecampane inulin is −32°. Schützenberger has also noticed considerable differences in the behaviour of the inulins from the two sources on treatment with acetic anhydride.

Little is known of the metallic derivatives of inulin. It is readily dissolved by a moderately concentrated solution of potassic or sodic hydrate, and on the addition of alcohol precipitates are obtained which apparently are metallic derivatives of inulin; the alkaline solutions do not alter Fehling's solution at ordinary temperatures, and even on heating for some time very little reduction takes place, so that inulin is not readily decomposed by alkalies. Baric hydrate, and an ammoniacal solution of normal plumbic acetate produce white precipitates in solutions of inulin, but the normal and basic acetate are without effect.

Inulin does not furnish a characteristic product on treatment with concentrated nitric acid; the dilute acid oxidises it to oxalic acid, but it is probable that saccharic acid is first formed. It does not reduce Fehling's solution. It is dissolved by concentrated sulphuric acid, and if care be taken to prevent rise of temperature, an almost colourless solution is obtained. The acetyl derivatives formed by the action of acetic anhydride on inulin have been very imperfectly examined; they are all amorphous bodies.

Inulin, unlike starch, is scarcely, if at all, affected by diastase or saliva, neither is it fermented by beer yeast; it undergoes decomposition very rapidly, however, under the influence of acids, and even mere boiling with water suffices to convert it into a body capable of reducing Fehling's solution.

It may be heated with water to between 90° and 100° (194° and 212° F.) for many hours without undergoing change, but on boiling the solution, the reducing substance is gradually produced, and by heating to 100° (212° F.) in sealed tubes it may apparently be completely converted into a lævoglucose: 10—15 grams of inulin undergoing this change if heated with 4—5 times their weight of water for 60—70 hours (Dragendorff). In the presence of acids, the decomposition takes place with much greater rapidity, being complete after a very few minutes' warming on the water bath, if the solution contain about 1 per cent. of hydrochloric or sulphuric acid.

According to Dubrunfaut (1856), the product of the action of water or acids on inulin is identical with sucrolævulose, but this conclusion, which has been generally adopted by chemists, appears to be based upon very insufficient evidence. He states that its apparent sp. rot. power is two and a half times as great as that of inulin itself: hence $[\alpha]_j = -44^\circ{\cdot}9 \times 2{\cdot}5 = -112^\circ{\cdot}25$; assuming the determination to have been made at the ordinary temperature, this value is somewhat higher than that assigned to sucrolævulose—viz., $[\alpha]_j = -106$ at 14° (57°·2 F.). According to Dragendorff, the product obtained by decomposing inulin by heating it with water,* if dissolved in cold water, has the apparent sp. rot. power $[\alpha]_D = -123^\circ$† at 21°—22° (69°·8—71°·6 F.), but if the solution be heated to about 60° (140° F.) and then cooled previous to the determination of its optical activity, the apparent sp. rot. power of the substance in solution sinks to about -83°. Sucrolævulose is not known to behave in this way.‡

Although the final product, lævoglucose is not the only product of the action of water on inulin, either alone or in presence of acids, but apparently a series of intermediate substances are formed just as in the case of starch. Thus, by heating inulin for only a short time with water, and precipitating the solution with alcohol, Dragendorff obtained a substance capable, like inulin, of forming sphœro-crystals, but easily soluble in cold water, and much more readily converted into lævoglucose by boiling with water; and which at first also is without action on Fehling's solution, but after 2—3 minutes' boiling begins to reduce it.* By heating for a longer time with water, a still more easily soluble body is produced, as in the previous case, together with lævoglucose, which can only be precipitated by the addition of a large quantity of alcohol to the very concentrated solution; when dried at 130° (266° F.), it has the same empirical composition as inulin, but is optically inactive, and apparently yields lævoglucose very readily when warmed with water. The substance thus obtained by Dragendorff, and which he states accompanies inulin in plants, exhibits a remarkable resemblance to Popp's synanthrose, which not improbably is a member of the $(C_6H_{10}O_5)_n$ group of carbohydrates, and not a body of the same empirical composition as cane sugar, as supposed by Popp. The same intermediate products are formed by the action of dilute acids, but their separation is much more difficult, on account of the readiness with which inulin undergoes alteration, and with which they are themselves altered, under the influence of acids.

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* In order to isolate the product, the solution is evaporated to a syrup, which is mixed with 4—5 vols. of absolute alcohol, the mixture allowed to stand for 24—48 hours, then filtered, the alcohol distilled off, the residue dissolved in a small quantity of water, the solution decolorised by animal charcoal, concentrated on the water bath, and the residue exposed over sulphuric acid.

† Dragendorff's observations were mostly made with a Wild polarimeter, illuminated by ordinary daylight, but in one case he determined the rotatory power of the same solution both for ordinary white light and for the yellow light of a sodium flame; and from the values obtained it would appear that his observations for white light may be reduced to values of $[\alpha]_D$ by division by 1·134.

‡ Krusemann (*Deut. chem. Ges. Ber.*, ix. 1465) finds that when inulin is heated with water in closed tubes, the rotatory power of the solution attains a maximum after a certain length of time, but then gradually falls as the heating is continued; this, however, is perhaps due to the alteration of the lævoglucose (*Comp.*, p. 602).

From the above, it will be evident that our knowledge of inulin and of its congeners is extremely imperfect, and that much has yet to be learnt, both with regard to the products of its decomposition by water, and also of the carbohydrates with which it is associated in plants. From the constant occurrence of starch in the leaves of plants which furnish inulin, it can scarcely be doubted that a genetic connexion exists between the two bodies, and as starch invariably yields dextrorotatory products when decomposed by artificial means, the study of the manner in which, perhaps, it is naturally converted into lævorotatory substances acquires especial interest.

(1575) GLYCOGEN: $(C_6H_{10}O_5)_n$.—This carbohydrate, which is only known to occur in animals, was discovered in 1857 by Claude Bernard (comp. *Ann. Chem. Phys.* [5], viii. 367). It appears to have a somewhat similar function to that fulfilled by starch and inulin in plants, and to be of great importance for cell growth, as it is found wherever this is actively going on. It is especially abundant in the liver of vertebrate animals during digestion, and also occurs in the muscles and in colourless blood

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[*] According to Popp (*Ann. Chem. Pharm.*, clvi. 190), if the expressed juice of *unripe* dahlia or artichoke tubers be precipitated with basic plumbic acetate, &c. (p. 636), a substance is obtained, which he terms *inuloid*, very closely resembling inulin in its properties, but considerably more soluble in water, and of lower specific gravity. When dried over sulphuric acid, it is a white amorphous body of the composition $C_6H_{10}O_5 + OH_2$, but is rendered anhydrous by heating at about 105° (221° F.); it has the apparent sp. rot. power $[\alpha]_j = 34^\circ{\cdot}5$ (calculated for the anhydrous substance), and on warming with acids yields a product of the apparent sp. rot. power $[\alpha]_j = -79^\circ$. It does not reduce Fehling's solution, but when it is boiled with it for some time a voluminous flocculent precipitate is obtained. It melts at about 130°—135° (266°—275° F.), and is decomposed at higher temperatures.

According to Dubrunfaut and Dragendorff the artichoke also contains a dextrorotatory carbohydrate.

corpuscles. In the fœtus, it is largely contained in the lungs, placenta and muscular tissue, but is almost if not entirely absent from the liver and other glands and the nervous system; after birth it is confined almost entirely to the liver and muscles. It occurs in considerable quantity in many mollusca, and has also been found in the larvæ of insects, and in the tapeworm of the pig. Apparently it is present in the liver, and in embryonic structures, in the solid state.

The amount of glycogen in the liver is greatest after a meal, but is quickly diminished by fasting, the diminution being due to its conversion into a glucose under the influence of an unorganised ferment present in the blood and in the liver itself. Although there is little doubt that glycogen is actually formed (chiefly) in the liver, it is uncertain from what materials it is produced, for not only is the amount increased by the use of food consisting chiefly of carbohydrates, but it continues to be formed in considerable quantity when the food consists of flesh alone. In the present imperfect state of our knowledge of the composition of flesh, however, we are not justified on this account in assuming that, even when the food consists of flesh alone, the glycogen is not more or less directly produced from carbohydrates, as it is by no means improbable that these latter are in a sense pre-existent in some at least of the albuminous substances which constitute flesh—*i.e.*, that they may be formed from them by simple hydration. The amount of glycogen in muscle is diminished by activity, but is not subject to such a rapid variation as the glycogen in the liver.

Preparation.—It is best prepared from liver, which must be that of a healthy animal killed an hour or so after a full meal, as otherwise the liver would contain but little glycogen. The animal (a large well-fed rabbit answers the purpose well) is rapidly killed by decapitation, the liver instantly removed, quickly chopped into pieces, and thrown into a quantity of briskly boiling water, where it is allowed to remain for a short time, the object being to raise the temperature of the liver as soon as possible to 100° (212° F.) in order to render the ferment which it contains inactive; the liquid is then poured off, the liver rubbed to a fine pulp, and again boiled with the water. The solution is now strained from the solid matter, filtered, and rapidly cooled by placing the vessel containing it in iced water. The albuminous substances dissolved in the liquid are best removed by Brücke's method, by the addition of a solution of potassic mercuric iodide, prepared by saturating a boiling solution of potassic iodide with mercuric iodide, this solution and hydrochloric acid being added alternately as long as a precipitate is produced; after standing a short time, the precipitate is removed by filtration, and the filtrate, whilst constantly stirred, mixed with sufficient 60 per cent. alcohol to cause a copious precipitate of glycogen. The precipitate is collected on a filter and washed with 60 per cent. alcohol, until the filtrate no longer produces a turbidity in a solution of potassic hydrate mixed with ammonia or ammonic chloride; it is then washed with 95 per cent. alcohol, afterwards extracted with ether in order to remove fatty substances, and finally dried in vacuo over sulphuric acid.

According to Bizio (*Compt. Rend.*, lxii. 675), pure glycogen may also readily be prepared from the mollusks *Cardium edule* and the oyster, the former yielding as much as 14, and the latter 9·5 per cent., calculated on the amount of dry substance they contain.

Pure glycogen is a snow-white, amorphous, tasteless substance, which, after drying at 100° (212° F.), has the composition $C_6H_{10}O_5$. It forms a paste with water, and rapidly dissolves in it on warming, yielding an opalescent solution, which becomes perfectly clear on the addition of potassic hydrate. It exerts a powerful dextrorotatory action on polarized light, its apparent sp. rot. power in aqueous solution being, according to Hoppe-Seyler, about three times as great as that of sucrodextrose. It is coloured reddish-brown by iodine. By the action of concentrated nitric acid, it is converted into a nitrate, whilst on boiling it with the dilute acid, oxalic acid is produced. It is not altered by moderately concentrated solutions of potassic or sodic hydrate, and does not reduce Fehling's solution.

By the action of dilute mineral acids, and of the unorganized ferment contained in malt extract, blood, liver, saliva, and the pancreatic secretion, glycogen is converted, first into a substance corresponding to dextrin, and then into a body capable of reducing Fehling's solution, which ferments in contact with beer yeast, is coloured brown by alkalies, and exerts a dextrorotatory action on polarized light (Bernard). According to Berthelot and Luca (1859, *Compt. Rend.*, xlix. 213), the body produced by the action of hydrochloric acid is identical with sucrodextrose, its compound with sodic chloride having precisely the same crystalline form and apparent sp. rot. power as that prepared from grape sugar, but they do not state that this conclusion is based on a direct comparison of the two compounds. Probably they contrasted their observations on the glycogen product with those of Pasteur, published a short time previously (1856), on the sodic chloride compound of the dextroglucose from diabetic urine, and as the identity of the latter with sucrodextrose is not yet proved with certainty (comp. p. 583), we must also for the present regard it as an open question whether the glucose from glycogen is sucrodextrose.

It is definitively established by Bernard's researches (*Ann. Chim. Phys.* [5], ix. 207) that the blood of both carnivorous and herbivorous animals, even after prolonged abstinence, contains a dextroglucose as one of its normal constituents. Bernard states that this glucose is identical with that present in diabetic urine; but this conclusion appears to be based merely on the qualitative reactions which the impure glucose from blood exhibits, and not on a comparison of the pure substances from the two sources.

The glucose rapidly disappears from the blood after death, and also on keeping the blood withdrawn from an animal, but its decomposition may be considerably retarded by the addition of a small quantity of glacial acetic acid; it is necessary, therefore, to estimate the glucose immediately after the blood is withdrawn from the animal: the method of doing this has been fully described by Bernard (*loc. cit.*, p. 228).

The results obtained by Bernard appear to show that the amount of glucose in blood is independent of the nature of the food; and also that blood contains a normal amount of glucose, even after the animal from which it is taken has been for a considerable time without food. Thus he found in the mixed blood of a healthy adult rabbit killed by decapitation 1·40 pts. per 1000; and in the carotid artery of a second similar animal 1·25 pts per 1000 of glucose. They had been fed on vegetables and bread, and were killed during the period of digestion; the stomach and intestines of both contained "sugar." Similarly, the blood of four healthy adult dogs in full digestion, which for some time previously had been fed entirely on cooked beef, contained 1·45, 1·32, 1·10, and 1·24 pts. per 1000 of glucose; no trace of sugar could be detected in the stomach or intestines of any of these animals. The venous blood of a healthy man, 60 years of age, partaking of a mixed diet, contained 1·17 pts. per 1000 of glucose. The blood of a dog which had for three days been entirely deprived of food contained 1·21 pts. per 1000 of glucose; while that of another dog in a feverish condition, which had been the subject of a physiological experiment, and which for two days previously had refused all food, contained 1·41 pts. per 1000 of glucose. The stomach and intestines of both of these animals were completely empty. The mixed blood of a rabbit which had been deprived of food contained 1·17 pts. per 1000 of glucose.

Although the amount of glucose in the mixed blood of animals is subject to considerable variation, under normal conditions it is comprised within the limits of 1 to 3 pts. per 1000 of blood: the presence of a less amount than 1 pt. per 1000 being an indication of deficient nutrition, while if the blood contain more than 3 pts. per 1000 the limit of saturation, so to speak, is exceeded, and glucose appears in the urine.

Arterial blood contains sensibly the same amount of glucose from whatever part of the system it be taken—viz., on an average from 1 to 1·5 pts. per 1000. Venous blood, on the contrary, contains varying amounts of glucose in different parts of the system, but usually a less amount than arterial blood—viz., from about ·6 to 1 pt. per 1000; that contained in the right side of the heart and the vena cava inferior above the point where the blood which has passed through the liver is poured into it, however, is much richer in glucose than the blood from any other part of the body. For example, Bernard found in blood drawn from the vena cava inferior at a point below the hepatic vein, 1·08 pts. per 1000 glucose, but 2·00 pts. per 1000 in blood drawn from the vena cava inferior of the same animal at a point level with the sub-hepatic veins. In another experiment the blood from different parts of the system was found to contain in 1000 pts. the following amount of glucose:

Blood from the right jugular vein	·91
Blood from the vena cava superior	·90
Blood from the right carotid artery	1·10
Blood from the right side of the heart	1·25

From these facts, it appears in the highest degree probable that the soluble carbohydrates which are either present in the food, or are formed from the insoluble carbohydrates during digestion (and also a portion of the albumenoids), do not directly pass into the general circulation, but that they are stored up in the liver in the form of glycogen; the latter then gradually undergoes conversion into glucose, and in this form is conveyed to the various parts of the system, where it is perhaps partially reconverted into glycogen (in the muscles), and partially undergoes alterations in other ways.

(1576) CELLULOSE: $(C_6H_{10}O_5)_n$.—This carbohydrate constitutes the essential part of the solid framework or cellular tissue of plants, but it apparently also exists in the animal kingdom, as the so-called tunicin contained in the outer envelopes of the *Tunicata* or *Ascidia,* according to Schœrer (*Ann. Chem. Pharm.*, clx. 312), is in all respects identical with vegetable cellulose. It occurs nearly pure in cotton, linen, elder pith, and in the pith of the *Aralia papyrifera,* from which *rice paper* is prepared; but as a rule, only the tissue of very young cells consists of pure cellulose, for as the plant grows the cell walls become incrusted with various matters. The following analyses of raw cotton, wheat and barley straw, and of a number of woods, afford illustrations of the extent to which cellulose is associated with other substances in various vegetable products:

—	Water.	Aqueous extract.	Alcohol-benzene extract.	Cellulose.	Incrusting substances.
Cotton . . .	7·00	·50	·40	91·35	·87
Barley straw .	11·75	9·34	1·99	49·22	27·70
Wheat straw .	10·39	8·52	1·58	49·17	30·34
Alder . . .	10·70	2·48	·87	54·62	31·33
Beech . . .	12·57	2·41	·41	45·47	39·14
Birch . . .	12·48	2·65	1·14	55·52	28·21
Black poplar .	12·10	2·88	1·37	62·77	20·88
Box	12·90	2·63	·63	48·14	35·70
Chestnut . .	12·03	5·41	1·10	52·64	28·82
Ebony . . .	9·40	9·99	2·54	29·99	48·08
Fir	13·87	1·26	·97	56·99	26·91
Lime . . .	10·10	3·56	3·93	53·09	29·32
Mahogany . .	12·39	9·91	1·02	49·07	27·61
Oak	13·12	12·20	·91	39·47	34·30
Scotch fir . .	12·87	4·05	1·63	53·27	28·18
Teak . . .	11·05	3·93	3·74	43·12	38·16
Willow . . .	11·66	2·65	1·23	55·72	28·74

The various matters which accompany cellulose in vegetable structures are usually included under the three heads of *ligneous matter, cork or cuticular substance,* and *intercellular substance.* Both ligneous matter and cork, the latter especially, are relatively richer in carbon and hydrogen than cellulose, but scarcely anything is known with certainty with regard to the nature of the numerous substances of which they are composed. The cuticular substance is distinguished from cellulose by its greater solubility in alkalies, and by being more readily destroyed by the action of nitric acid, chlorine, &c.; cork especially is characterized by its behaviour on oxidation with nitric acid, which converts it into an acid of the succinic series, suberic acid, $C_8H_{14}O_4$. Ligneous matter also opposes less resistance to the action of reagents than cellulose, and is converted without difficulty by the action of chlorine and similar agents into substances soluble in dilute alkalies, and partly even in water and alcohol. The intercellular substance in some cases consists of so-called pectous and mucilaginous bodies, and in others exhibits the characters of ligneous matter. For a full description of the formation of cellular tissue in plants, and of the manner in which the cellulose becomes incrusted with various matters, the student is referred to Sachs's "Text-Book of Botany." It may here be pointed out that we are also ignorant of the nature of the so-called *humus* substances which are formed by the gradual decay of vegetable matter and of woody fibre; the crude products have been analysed by Mulder and others, and formulæ have even been attributed to them, but as they are entirely devoid of distinctive properties, and do not admit of separation and purification by any of the methods at present known, the results which have been obtained are of very little value. From Pasteur's experiments it appears that the decay of vegetable substances, and indeed of organic matters generally, is neither a spontaneous process nor merely the result of slow oxidation at the expense of atmospheric oxygen, but that it is in great part at least due to the mediation of low organisms, the germs of which are present in the atmosphere; thus he has found, for example, that when moistened sawdust is exposed to a current of air it generates carbonic anhydride abundantly, whereas if it be previously heated to destroy the germs, and every precaution be taken to remove them from the apparatus in which the experiment is carried out, and from the air, no appreciable oxidation takes place.

Estimation of Cellulose.—The analyses above given are taken from Dr. Hugo Müller's article (150 pp.): *Die Pflanzenfaser und ihre Aufbereitung für die Technik*, in Hofmann's *Bericht über die Entwickelung der chemischen Industrie während des letzten Jahrzehends* (1877). In this most valuable work an account is given of the various materials in use for the manufacture of paper, and of the modes of treating them, and also of a large number of other cellulose-yielding vegetable substances.

The method employed by Dr. Müller for estimating the cellulose is one devised by himself, and as it appears to possess some advantages over that of Schulze, which has hitherto been generally adopted, it may here be described. About 2 grams of the material to be examined are dried at 110°—115° (230°—239° F.), and if it contain any considerable quantity of fat, wax, or resin, it is first exhausted with a mixture of strong alcohol and benzene, and then extracted by boiling several times with water, or very dilute ammonia. The softened mass, if not already sufficiently divided, is next triturated in a mortar with a boxwood pestle; in the case of woods, however, if fine shavings be employed, further division in this manner is unnecessary. It is now transferred, with 100 cc. of water, to a capacious wide-mouthed stoppered bottle, and 5 or 10 cc. of an aqueous solution of bromine, containing 2 cc. of the latter in 500 cc. of water, are added according to the nature of the material. In the case of the purer bark fibres, such as flax and hemp, the yellow colour of the liquid only slowly disappears, but with straw and woods it disappears in a very few minutes. When this happens, a fresh quantity of the bromine solution is added, and the addition of bromine is repeated until at last the liquid retains its yellow colour, and bromine can still be detected in it, after standing 12—24 hours. The substance is now filtered from the liquid, washed with water, and heated nearly to boiling with about 500 cc. of water to which 2 cc. of liquid ammonia are added; this causes all crude vegetable fibres and woods to assume a more or less intense dark brown colour, and the liquid is similarly coloured. The undissolved matter is then separated by filtration, washed, returned to the bottle, again treated with bromine solution as before, and when the action of the bromine is completed, exhausted with dilute ammonia. A second treatment is usually sufficient in the case of the purer bark fibres, but tissues which are more completely lignified require a third and even fourth treatment in order to free the cellulose completely from foreign substances. The operation may be considered to be at an end when, after standing 24 hours with very dilute bromine solution, on treating the washed residue with warm dilute ammonia, the liquid is no longer coloured. By this treatment the vegetable tissue gradually becomes disintegrated, and finally, after washing with water and then with boiling alcohol, a brilliant white mass of isolated cells is obtained. This is dried and weighed.

In order to ascertain the amount of the other substances which accompany cellulose—viz., of the substances soluble in water, of fatty, resinous, and waxy matters, of pectous-like substances, and of incrusting matters, five grams of the comminuted tissue are extracted by boiling five times with water, using 100 cc. each time, and then dried; they are next exhausted with a mixture of benzene and alcohol, which removes fat, wax, &c.; then the residue is several times boiled with dilute ammonia, which, in most cases, dissolves a considerable quantity of colouring matter and of pectous substances, the amount of which may be estimated by evaporating the solution to dryness; and finally, the mass is submitted to the treatment with bromine, &c., above described. After the cellulose has been dried and weighed, it may be four or five times boiled (each time with 100 cc.) of a 1 per cent. solution of crystallized sodic carbonate, and from the loss of weight which it suffers, the amount of the more soluble modification of cellulose present in most vegetable fibres may be approximately determined.

Cellulose bears a very close genetic relation to starch, being in all probability more or less directly formed from it; but it is a much more stable substance, and is not, like starch, readily rendered soluble. Nevertheless it is undoubtedly in some cases deposited as a reserve material, as in the endosperm of the date for example, the greater part of the hard kernel of which consists of cellulose, which is gradually dissolved during germination; the mucilaginous substances which are met with in certain plants, and some at least of the substances which cause lignification and cuticularisation are perhaps also products of the partial alteration of the cellulose of the cell walls.

Pure cellulose may readily be obtained from any of the purer forms in which it occurs naturally, such as cotton or elder pith, or from unsized paper or old linen, by submitting them to the action of bromine, &c., in the manner above described.

Cellulose is a white, odourless, tasteless, very hygroscopic substance, of the sp. gr. about 1·45, insoluble in all ordinary menstrua; the only liquid apparently in which it is soluble without change is a solution of cuprammonic hydrate.

This solution is most conveniently prepared by dissolving cupric hydrate to saturation in ammonia, the cupric hydrate for this purpose being precipitated from a solution of cupric sulphate in presence of ammonic chloride by sodic hydrate, well washed by decantation and then on a filter, and preserved under water. If cotton wool or paper be placed in contact with this solution, it assumes a gelatinous condition, and on agitation gradually dissolves, forming a viscid solution, which may be filtered after dilution with water. On neutralizing the filtrate with hydrochloric acid, the cellulose separates as a gelatinous precipitate resembling aluminic hydrate, which, when dried, forms a transparent, brittle, horn-like mass; it may also be precipitated by carbonic anhydride and by many neutral substances, such as sugar or sodic chloride, and even water in large quantity causes its gradual separation. Cellular tissue, as a rule, however, is not directly soluble in the cuprammonic hydrate solution, but may be rendered soluble, in some cases by mere drying at about 150° (302° F.), or by boiling with water, and in others by treatment with dilute alkaline and acid solutions; highly lignified tissue becomes soluble only after treatment with oxidizing agents, &c.

Cellulose is not coloured by iodine solution alone, or at most assumes a yellow or brownish colour, but in presence of hydriodic acid, potassic or zincic iodide, sulphuric or phosphoric acid, and zincic chloride it is coloured blue by iodine; concentrated sulphuric acid and a concentrated solution of zincic chloride especially favour the production of the blue colour. These substances apparently do not act by removing impurities, or by causing the cellulose to swell up with water, for if a portion of cellular tissue be treated with any one of the reagents which induce the blue colour, and be then freed from it by washing, it is not then coloured blue by iodine; and cotton wool, for example, which has been boiled with dilute hydrochloric or nitric acid, or dissolved in cuprammonic hydrate, neutralized and washed, is also not coloured.

Cellulose has but a very slight tendency to form metallic derivatives.

It is not appreciably altered by cold moderately concentrated solutions of potassic or sodic hydrate, but in very concentrated solutions it swells up and gradually dissolves; apparently the liquid at first contains unaltered cellulose, (perhaps in the form of a potassic derivative), which may be precipitated by the addition of water, but it is said that alteration soon takes place, and that at first a substance is produced which is coloured blue by iodine, then a dextrin-like substance, and finally a glucose. Cellulose (in the form of filter paper) has the property of absorbing an appreciable amount of baric hydrate from dilute solutions of the latter, from which it cannot be freed by washing with water (Müller, *Zeit. anal. Chem.*, i. 84). It appears also to form plumbic derivatives (Mulder, *Jahresb.* 1863, 565). Its dissolution in a solution of cuprammonic hydrate is not improbably due to the formation of a metallic derivative.

If cotton wool or Swedish filter paper be heated at 180° (356° F.) for 1-2 hours with 6-8 pts. acetic anhydride, it is entirely dissolved and converted into the triacetate, $C_6H_7(C_2H_3O_2)O_2$, which may be separated by pouring the syrup into water; in the pure state, it is a white powder, soluble in glacial acetic acid and concentrated sulphuric acid, and is very easily converted into cellulose and acetate by boiling with dilute alkali. The acetic acid solution is entirely without action on polarized light. It is not possible to obtain higher derivatives by the action of a greater excess of the anhydride at higher temperatures; at lower temperatures the cellulose merely swells up in the anhydride without dissolving, forming lower acetates which cannot be separated from the unaltered substance (Schützenberger, *Ann. Chem. Pharm.*, clx. 75).

Corresponding nitrates are formed by the action of nitric acid, and constitute the well-known substances *gun cotton* and *collodion*. If a mixture of nitric and sulphuric acids, each in the highest degree of concentration, be employed, the cellulose is converted into the trinitrate, $C_6H_7(NO_3)_3O_2$, but by the action of acid mixtures containing larger proportions of water, lower nitrates are produced, which, according to Hadow (*Journ. Chem. Soc.*, 1854, vii. 208), are represented by the formulæ $C_{18}H_{22}(NO_3)_8O_7$ and $C_{18}H_{23}(NO_3)_7O_8$. The trinitrate is highly explosive, soluble in ethylic acetate, but insoluble in any mixture of ether and alcohol; properly manufactured gun cotton consists almost entirely of this substance. The compound $C_{18}H_{22}(NO_3)_8O_7$ is less explosive, and insoluble in acetic acid, but soluble in a mixture of seven parts of ether and one part of alcohol, whereas the compound $C_{18}H_{23}(NO_3)_7O_8$ is largely soluble both in ether and in glacial acetic acid; ordinary collodion is a mixture of these two substances, but the former, according to Hadow, is the best fitted for photographic purposes. These nitrates scarcely differ from the unchanged cellulose in appearance, but if pyroxylin (gun cotton) prepared from ordinary cotton be examined by the microscope in polarized light it is found to have lost the property of depolarization which cotton possesses. A solution of collodion has a dextrorotatory action on polarized light, cellulose itself being apparently an optically inactive substance. These nitrates may be reconverted into cellulose by digestion at ordinary temperatures with an alcoholic solution of potassic sulphydrate, or by the action of ferrous chloride: they are also freely dissolved by an aqueous solution of potassic hydrate, by which they are decomposed. A full account of an inquiry into the processes of manufacture, the composition, and the causes which influence the stability of gun cotton, and into its behaviour as an explosive agent, will be found in Abel's papers, *Phil. Trans.*, 1866, 269; 1867, 181; 1869, 489; and 1874, 337.

Cellulose is gradually altered by prolonged boiling with dilute hydrochloric or sulphuric acid, but it does not entirely withstand the action of boiling water alone, and at higher temperatures it is decomposed by water without difficulty. Thus, according to Hoppe-Seyler (*Deut. chem. Ges. Ber.*, iv. 15), if Swedish filtering paper be heated with water at 200° (392° F.), for 4—6 hours, it becomes browned, while the liquid assumes a yellow colour, and contains glistening particles and brown substances in suspension; on opening the tubes carbonic anhydride escapes, and the solution contains no inconsiderable quantity of formic acid and pyrocatechol.

Concentrated hydrochloric and sulphuric acids dissolve cellulose, and are said to convert it, in the first instance, into a substance which is coloured blue by iodine alone, and swells up considerably in water, but without dissolving; a soluble "modification of cellulose" is next formed, together with a dextrin-like substance, having a less powerful dextrorotatory action on polarized light than starch dextrin, and if the solution be largely diluted with water and boiled, a glucose is formed. We have no certain knowledge of any of these products, however, for none of them have been examined in the pure state. Girard has recently stated (*Ann. Chim. Phys.* [5], ix. 116) that, if purified cotton wool be immersed for twelve hours in sulphuric acid of 45° Beaumé, it does not appreciably alter in appearance, but if it be perfectly freed from acid by washing, and dried at a low temperature, it forms a friable mass which, if rubbed between the fingers, at once becomes reduced to a snowy white powder; this product, according to Girard, has the composition $C_{12}H_{22}O_{11}$, being formed from cellulose by the fixation of the elements of water, and may therefore be termed *hydrocellulose*. It is said to retain this composition after desiccation (at what temperature is not stated); if heated for several days to 50° (122° F.), it gradually absorbs oxygen, and assumes a yellow colour, and on treating it with water a residue of the unaltered substance is obtained, and a yellow solution, which reduces Fehling's liquid; it is also slowly dissolved and decomposed on digestion with a 1 per cent. solution of potassic hydrate.

When unsized paper is plunged for a few seconds into a mixture of equal volumes of concentrated sulphuric acid and water, then washed, first with water, then with dilute ammonia, and lastly with water again, it acquires considerable toughness, in consequence apparently of the conversion of the outer surface of cellulose into a substance by which the fibres are cemented together. A concentrated solution of zincic chloride has a similar action. Paper thus prepared is known under the name of vegetable parchment, from its resemblance to parchment in toughness and appearance; it has many practical uses, and may be substituted for bladder as a septum for dialysis.

Cellulose is gradually altered by prolonged boiling with alkalies, but much less readily than by acids. It is said that if it be heated with potassic hydrate at 160° (320° F.), and the mass be dissolved in water, a solution is obtained from which acids precipitate a substance having the general properties of cellulose, but which is soluble even in cold solutions of alkalies. According to Peligot, if cellulose moistened with water be submitted to distillation with an equal weight of potassic hydrate, methylic alcohol distils over, and the residue contains potassic oxalate. A large amount of oxalate is also formed on heating cellulose with a mixture of potassic and sodic hydrates; this reaction, in fact, is made use of for the preparation of oxalic acid on the large scale (q. v.).

When subjected to destructive distillation, cellulose yields a considerable amount of carbonaceous matter, together with carbonic anhydride, methane, methylic alcohol, and acetic acid as chief products; pyrocatechol is also formed, and doubtless other substances are produced. It is scarcely necessary to point out that the products of the destructive distillation of wood are only in part derived from cellulose.

Little is known of the behaviour of cellulose with oxidizing agents. It yields oxalic acid in abundance when boiled with moderately concentrated nitric acid; it is slowly oxidized by chlorine in presence of water, and also by bleaching powder solution, and on treatment with a concentrated solution of the latter yields a small amount of carbonic anhydride, together with a syrupy mixture of substances, partly possessed of acid characters, soluble in water (Hugo Müller). It is also slowly oxidized in contact with ferric and manganic oxides; hence the destruction of cotton and linen fabrics by rust spots.

Gums—Pectous Substances—Vegetable Mucilage.

These terms are applied to a variety of vegetable products of the nature of which at present very little is known; they probably, however, all belong to the class of carbohydrates: *i.e.*, they are compounds of carbon, hydrogen and oxygen containing either six, or some simple multiple of six, atoms of carbon in their molecules, the hydrogen and oxygen being present in the same relative proportions as in water.

(1577) ARABIN, METARABIN, PARARABIN.—According to the researches of Scheibler (*Deut. chem. Ges. Ber.*, 1868, i. 58 and 108; 1873, vi. 612) and Reichardt (*ibid.*, 1875, viii. 807), fleshy roots, such as the sugar beet and carrot, contain two carbohydrates, metarabin and pararabin, insoluble in water, which may be rendered soluble, the former by alkalies and the latter by acids; pararabin is apparently not altered by this treatment, but metarabin is converted into soluble arabin, which may also be formed from pararabin by heating it with alkali. The following method of preparing arabin from sugar beet is recommended by Scheibler:—The fresh pulp having been freed as completely as possible from the juice by pressure, the press-cake is broken into fragments, and immersed for several hours in alcohol (86—90 per cent. Tr.); the alcoholic solution is then expressed, and the residue again similarly treated. The soluble substances are thus almost completely removed. The dry mass is now thrown into boiling water and heated with it for a short time; milk of lime is then added to strong alkaline reaction, and the whole heated for some time in the water bath. The solution is then separated, the dissolved calcic hydrate precipitated by carbonic anhydride, the filtrate evaporated to a small bulk in the water bath, then filtered, rendered strongly acid with acetic acid, and precipitated with a large excess of strong alcohol. After a time, the solution is poured off, the precipitate dissolved in a small quantity of water, the liquid filtered, if necessary, and again precipitated with alcohol; these operations are several times repeated. Finally, the product is dissolved in a small quantity of water, and sufficient alcohol added to the solution to precipitate only a small proportion of the arabin; after standing several days, the clear liquid is syphoned off from the deposit, which contains most of the impurities, and the arabin remaining in solution is precipitated by alcohol. It cannot, however, be entirely freed from ash constituents in this manner. The amount of arabin in beet varies greatly in different seasons.

When dry, arabin thus prepared has the composition $C_{12}H_{22}O_{11}$,* and in most of its properties exhibits the closest resemblance to purified gum arabic. Its solutions in water have about the same sp. gr. as solutions of cane sugar of the same strength. It does not reduce Fehling's solution. Most frequently it exerts a powerful lævrorotatory action on polarized light, but occasionally the product obtained in the manner above described has a slight dextrorotatory action. It undergoes inversion when heated with dilute sulphuric acid, the solution acquiring the property of reducing cupric salts, and of deviating the plane of polarization powerfully to the right; the product consists of arabinose (1560) and a glucose (?) which has not yet been isolated in the pure state, but is apparently of lower rotatory power.

Pararabin is prepared from beet or carrot pulp, freed from all soluble matters by lixiviation with water and alcohol, by digesting it for some hours with a 1 per cent. solution of hydrochloric acid, then heating to boiling, and precipitating the expressed liquid with alcohol; it separates as a gelatinous mass, or in flocculi. The precipitate is completely freed from acid by washing with alcohol, and then dried at 100° (212° F.). It is a white pulverulent substance, of the same composition as arabin, which swells up in water, and dissolves on heating or on the addition of an acid, but is reprecipitated by alcohol and by alkalies. It is not converted into arabinose by the action of acids, but on warming it with an alkali it is gradually dissolved and converted into a substance having all the properties of arabin, amongst others, that of yielding arabinose when acted upon by acids (Reichardt).

Gum Arabic.—This substance is the dried exudation from the bark of various species of *Acacieæ* growing in Arabia, Egypt, Senegambia, &c. The appearance of gum is too well known to need description; it dissolves very slowly in about an equal weight of water at ordinary temperatures, forming a thick, glutinous, slightly opalescent liquid, having a mawkish taste: it is a colloid substance, diffusing with extreme slowness through parchment paper, and organized membranes. Even the most carefully selected pieces of gum arabic yield from 2·7 to 4 per cent. of ash on incineration, consisting mainly of calcic carbonate, but containing also magnesic and potassic carbonates; by repeatedly precipitating a solution of gum in water acidulated with hydrochloric or acetic acid with alcohol, it may, however, be almost entirely deprived of mineral matters. According to Neubauer, gum thus purified and perfectly freed from acid by washing with alcohol, is a milk-white amorphous substance, which as long as it remains moist dissolves easily in water, forming a distinctly acid solution, having the power of liberating carbonic anhydride from sodic carbonate; the solution is not precipitated by pure alcohol, but the addition of the merest trace of an acid or of a salt is sufficient to determine the separation of the gum; it is not precipitated by normal or basic plumbic acetate, except in presence of ammonia. After the gum has been perfectly dried, either in the air or at 100° (212° F.), it is no longer soluble, even in hot water, merely swelling up in it to a gelatinous mass, but if baric, calcic, potassic or sodic hydrate be added, it gradually dissolves, forming a solution which is indistinguishable from ordinary gum: ordinary gum, in fact, apparently consists of calcic, magnesic, &c., derivatives of the substances which constitute the purified gum. Gum may also be purified from mineral substances by submitting a concentrated solution, acidulated with about 5 per cent. of hydrochloric acid, to dialysis, stopping the process when the whole of the acid has passed through the dialyser. According to Barfoed (*Journ. pr. Chem.* [2], xi. 186), the conversion of the soluble modification of purified gum into the insoluble variety depends not only upon its purity and state of dryness, but also on the treatment to which the ordinary gum employed has been previously submitted. It takes place more readily when the gum is heated in the dry state before dissolving it in water, and less readily if the solution of gum has been kept for a considerable time, or has been warmed, before adding acid and precipitating with alcohol; in fact, purified gum prepared from a solution of gum arabic which has been kept for twenty-four hours at the temperature of boiling water may be dried at 100° (212° F.) without becoming insoluble, but is converted into the insoluble modification at higher temperatures.

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* The properties of arabin are so totally different from those of cane sugar and its congeners that it may be doubted whether this formula really expresses its composition; it much more nearly resembles the dextrins in its properties. Scheibler does not state at what temperature his arabin was dried.

When oxidized by moderately dilute nitric acid, gum arabic yields mucic and saccharic acids and oxidation products of these latter. By heating it with water and bromine at 100° (212° F.), and neutralizing the solution with argentic hydrate, &c., Hlasiwetz and Barth (*Ann. Chem. Pharm.*, cxxii. 110) obtained an acid having the same composition and the properties of the acid formed in a similar manner from milk sugar (p. 611), with the exception that its rotatory power was slightly greater.

If it be heated with twice its weight of acetic anhydride at 150° (302° F.), gum arabic does not dissolve, but is converted into a substance which after washing with boiling water, and then with alcohol, forms a white amorphous powder, which is converted by alkalies into soluble gum; it has the composition $C_6H_8(C_2H_3O_2)_2O_3$. By heating at 180° (356° F.) with a greater excess of the anhydride, a pentacetate, $C_{12}H_{15}(C_2H_3O_2)O_5$, having similar properties, is formed (Schützenberger, *ibid.*, clx. 80). Although gum exhibits marked acid characters, the number of hydrogen atoms in it which can be displaced by metals is very small; thus, according to Neubauer, the calcium derivative formed by boiling a solution of purified gum with excess of calcic hydrate, and precipitating with alcohol, when dried at 100° (212° F.), has the composition $CaO(C_6H_{10}O_5)_4$.

Purified gum arabic dried at 100° (212° F.) has the composition $C_{12}H_{22}O_{11}$, but judging from its properties, it is not improbable that it is incompletely deprived of the water of hydration at this temperature, and that in the anhydrous state its composition is represented by the formula $(C_6H_{10}O_5)_n$. It is undoubtedly a mixture of several carbohydrates. According to Scheibler (*Deut. chem. Ges. Ber.*, vi. 612), it yields the same products as sugar beet arabin on treatment with sulphuric acid, but the various kinds furnish different amounts of arabinose, and also act differently on the polarized ray both before and after inversion. The results which Scheibler obtained in the case of a number of samples of commercial gum arabic are exhibited in the following table:

Description.	Per cent. of ashes.	Apparent sp. rot. power $[\alpha]_j=$	After inversion.	
			Apparent sp. rot. power.	Cupric oxide, red. power of prod. from 100 pts.
Gum Arab. Levantine nat. . . .	3·50	−29°·2	+46°·1	60·0
„ „ Levantine elect. . . .	3·50	−30°·0	+36°·9	53·4
„ „ Sennary elect. . . .	2·79	+37°·3	+54°·6	48·3
„ „ Sennary in granis . .	3·24	+46°·1	+73°·8	50·9
„ Senegal de fleuve	4·44	−28°·8	+38°·5	61·1
Purified gum Arabic	·34	+42°·4	+83°·5	79·1

A relatively much larger amount of arabinose is obtained from sugar beet arabin than from gum arabic, some specimens of which furnish very little arabinose, but a large quantity of a syrupy "sugar;" it has not yet been shown, however, that this latter is the same whether obtained from sugar beet arabin or from gum arabic arabin, so that at present it is but a mere guess to say that the various arabins are mixtures of the same constituents in different proportions.

To prepare arabinose, arabin or gum arabic is heated with dilute sulphuric acid for 2—3 hours on the water bath, the solution is then neutralized with baric carbonate, the filtrate evaporated to a syrup, and mixed with 2—3 vols. of 90 per cent. alcohol; the alcohol is then distilled off from the filtrate, and the residue concentrated to a syrup. The arabinose gradually crystallizes from this syrup, and is purified by recrystallization; its separation may be facilitated by the addition of a few crystals of arabinose.

Cherry tree and Bassora gum, and gum tragacanth, which are only partially soluble in water, are apparently mixtures of bodies either identical with, or very closely allied to, the soluble and insoluble modifications of gum in the so-called arabin and metarabin, but very little is known of their chemical behaviour (comp. Giraud, *Compt. Rend.* lxxx. 477). Gum tragacanth is the exudation from the stem of several species of *Astragalus*; according to Von Mohl and Wigand's investigations, it is not simply the dried juice of the plant, but is produced by a metamorphosis of the cellular tissue, and hence there can be little doubt of its close genetic relation to cellulose.

Pectous Substances.—This name has been given to a number of amorphous uncrystallizable substances extracted from plant tissues by boiling with water, or with dilute acids or alkalies; but in all probability the bodies which have long been known by this name, and to which Fremy in 1848 assigned formulæ which represent them as containing relatively much less hydrogen than the carbohydrates, judging from the manner in which they have been prepared and from the descriptions given of their properties, are in reality carbohydrates, and identical with the substances previously described as parabin, metarabin, and arabin.

Vegetable Mucilage.—At present little is known of the substances present in such large quantities in many seeds, such as linseed and quince-seed, in the roots of the marshmallow, in the tubers of various species of *Orchis*, &c., which swell up with water to a thick mucilage. Purified linseed mucilage apparently has the empirical composition $C_6H_{10}O_5$; on boiling it with dilute sulphuric acid, a body capable of reducing Fehling's solution, and a gum-like substance are produced (Kirchner and Tollens, *Ann. Chem. Pharm.*, clxxv. 205). Quince-seed mucilage also yields these substances when boiled with sulphuric acid, but together with a considerable quantity of cellulose; Kirchner and Tollens regard this latter as a distinct product of the action of the acid, and not as a mere mechanical impurity (comp. Sachsse, *op. cit.*).

Constitution of the Carbohydrates.

(1578) It will be evident from the foregoing description of the various carbohydrates that our knowledge of most of them is extremely imperfect; nevertheless, sufficient has already been learnt to enable us with much probability to predicate the probable character of the relations which obtain between the more important members of the group.

Judging from their properties, it appears in the highest degree probable that all the carbohydrates, with the exception of the glucoses, contain a greater number of carbon atoms in their molecules than these latter; there can be no doubt moreover, that if the molecular composition of the glucoses be represented by the formula $C_6H_{12}O_6$, that of the higher carbohydrates, as we may term the members of the $C_{12}H_{22}O_{11}$ and $(C_6H_{10}O_5)_n$ groups, must be expressed by formulæ containing some simple whole multiple of six atoms of carbon.

The conclusion that the molecular composition of the glucoses is expressed by the formula $C_6H_{12}O_6$ necessarily follows from their relation to the hexhydric alcohols mannitol and dulcitol,* which are derived from the paraffin—normal hexane (1546), C_6H_{14}. The conversion of the glucoses into these alcohols, however, also serves to prove that the six atoms of carbon in the former must be regarded as being in direct association with each other: while, on the other hand, from the extreme readiness with which the higher carbohydrates are ultimately converted into glucoses by mere hydration, it must be supposed that the several C_6 groups which enter into their composition are but indirectly associated together by means of oxygen, after the manner of the hydrocarbon radicles in ordinary ether for example, $C_2H_5.O.C_2H_5$.

There is little, if any, positive evidence as to the number of C_6 groups which are thus associated together in the various higher carbohydrates. The simplest and apparently most probable hypothesis in the case of the saccharons or carbohydrates similar in composition to cane sugar is that they are formed from two molecules of glucose by the withdrawal of the elements of a single molecule of water, and that therefore the formula $C_{12}H_{22}O_{11}$ does not merely express their empirical, but also their molecular, composition: the formulæ of the two classes of compounds would on this view be as follows:

$$C_6H_{12}O_6 \qquad\qquad \left.\begin{matrix}C_6H_{11}O_5\\C_6H_{11}O_5\end{matrix}\right\}O$$

Glucoses. Saccharons.

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* Müntz and Aubin (*Compt. Rend.*, lxxxiii. 1213) have recently established the identity of the mannitols obtained by the action of nascent hydrogen on, (*a*) the optically inactive glucose prepared by heating cane sugar with a small quantity of water at 160°(320° F.), (*b*) the mixture of lævulose and dextrose formed on inversion of cane sugar by acids, (*c*) sucrodextrose, (*d*) sucrolævulose, and (*e*) lævoglucose from inulin. The method they adopted is founded on the fact that although mannitol alone is almost without action on polarized light, many of its derivatives exhibit considerable optical activity. The deviation (in scale divisions) caused, 1. by an aqueous solution containing 10 grams of mannitol alone in 100 cc., 2. by a solution containing the same amount of mannitol plus 12·8 grams of borax, 3. by a solution containing 8 grams of mannitol and 8 grams of sodic hydrate in 100 cc., and 4. by a solution of 3 grams of the hexnitrate in 100 cc. of anhydrous alcohol, were as follows:

—	Mannitol alone.	Mannitol and borax.	Mannitol and NaOH.	Mannitol hexnitrate.
Mannitol from inactive glucose . . .	− 0·2	+ 23·1	− 3·7	+ 12·7
„ „ invert sugar	− 0·2	+ 22·0	− 3·5	+ 12·7
„ „ pure sucrodextrose . .	− 0·1	+ 23·0	− 3·4	+ 12·3
„ „ pure sucrolævulose . .	− 0·1	+ 21·6	− 3·2	+ 12·5
„ „ inulin glucose	− 0·0	+ 22·0	− 3·2	+ 12·3

We may here call attention to the fact that all the carbohydrates whose composition has been definitely ascertained to be that expressed by the formula $C_{12}H_{22}H_{11}$ are very soluble crystalline substances, which readily diffuse through colloid septa, and it is a question as to whether these properties may not be considered to be characteristic of all carbohydrates having the same molecular composition as cane sugar. It is true that the formula $C_{12}H_{22}O_{11}$ has been assigned to two bodies, which, although very soluble in water, are amorphous, and belong to the class of colloid substances—viz., synanthrose and arabin, and also to cellulose, which is an amorphous insoluble substance: but these compounds have been very insufficiently studied, so that it is by no means unlikely that they may prove to be carbohydrates of the composition $(C_6H_{10}O_5)_n$, all of which appear to be colloid substances. But even if the empirical composition of the two first mentioned be correctly represented by the formula $C_{12}H_{22}O_{11}$, they are probably bodies of higher molecular weight than cane sugar.

The carbohydrates of which amylin (dextrin) is the type, certainly contain as many carbon atoms in their molecules as the saccharons, since amylin, $(C_6H_{10}O_5)_n$, is converted into amylon, $C_{12}H_{22}O_{11}$, by mere hydration; but the fact that the saccharons are crystalline, *highly diffusible* substances, whereas amylin is an amorphous *colloid* body, favours the assumption that the molecule of amylin is more complex, and that it contains at least twice as many carbon atoms as that of amylon. According as amylin is regarded as derived from a single molecule, or from two molecules, of amylon, it may be represented by either of the following formulæ:

$$O\left\{\begin{matrix} C_6H_{10}O_4 \\ C_6H_{10}O_4 \end{matrix}\right\}O \qquad\qquad O\left\{\begin{matrix} C_6H_{10}O_4.O.C_6H_{10}O_4 \\ C_6H_{10}O_4.O.C_6H_{10}O_4 \end{matrix}\right\}O$$

From the results obtained by O'Sullivan, there can be but little doubt that starch has a very high molecular weight, and judging from the proportions in which amylon and amylin are formed by the action of malt extract at different temperatures, the most probable assumption would appear to be that it contains either 72 or 144 atoms of carbon in its molecule, according as we regard amylin as $C_{12}H_{20}H_{10}$ or $C_{24}H_{40}O_{20}$. On the former assumption, its decomposition at temperatures below 63°, between 64° and 68°—70°, and above 68°—70° C., is represented by the following equations:

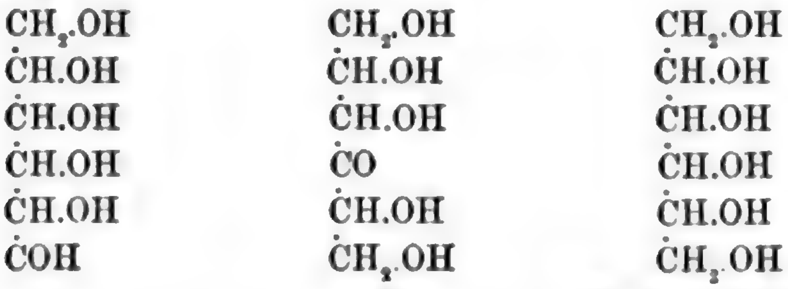
$$\begin{aligned} C_{72}H_{120}O_{60} + 4OH_2 &= 4C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}. \\ C_{72}H_{120}O_{60} + 2OH_2 &= 2C_{12}H_{22}O_{11} + 4C_{12}H_{20}O_{10}. \\ C_{72}H_{120}O_{60} + OH_2 &= C_{12}H_{22}O_{11} + 5C_{12}H_{20}O_{10}. \end{aligned}$$

whereas on the latter assumption we have the following:

$$\begin{aligned} C_{144}H_{240}O_{120} + 8OH_2 &= 8C_{12}H_{22}O_{11} + 2C_{24}H_{40}O_{20}. \\ C_{144}H_{240}O_{120} + 4OH_2 &= 4C_{12}H_{22}O_{11} + 4C_{24}H_{40}O_{20}. \\ C_{144}H_{240}O_{120} + 2OH_2 &= 2C_{12}H_{22}O_{11} + 5C_{24}H_{40}O_{20}. \end{aligned}$$

There is no evidence by which we can form an estimate of the molecular weight of the remaining carbohydrates of the same empirical composition as starch; from their physical properties and behaviour under various circumstances, however, it would appear probable that glycogen and inulin are bodies of lower, and cellulose a body of higher, molecular weight than starch.

It now remains to consider the "constitution" of the glucoses or carbohydrates of the composition $C_6H_{12}O_6$. From their general behaviour there can be no doubt that they are closely related to the hexhydric alcohols dulcitol and mannitol, into which several have already been converted by the action of nascent hydrogen; it will be remembered that we have pointed out that these two alcohols are both represented by the same formula (p. 559). The conversion of sucrodextrose into the compound $C_6H_7ClO(C_2H_3O_2)_4$ by the action of acetic chloride, and the formation from the latter of the compound $C_6H_7O(NO_3)(C_2H_3O_2)_4$ by the action of nitric acid (p. 580), indicates that it must be regarded as a pentahydroxyl derivative; and the conversion of cane and milk sugar into octacetates (pp. 600, 610) by the action of acetic anhydride serves in a similar manner to prove that sucrolævulose and the dextroglucoses furnished by milk sugar on inversion are also pentahydroxyl derivatives. The only formulæ, however, which can be assigned to a body convertible like sucrodextrose into mannitol (or dulcitol) by the addition to it of two atoms of hydrogen, and containing *five* hydroxyl groups, are the following:



$$\begin{array}{lll} CH_2.OH & CH_2.OH & CH_2.OH \\ \dot{C}H.OH & \dot{C}H.OH & \dot{C}H.OH \\ \dot{C}H.OH & \dot{C}H.OH & \dot{C}H.OH \\ \dot{C}H.OH & \dot{C}O & \dot{C}H.OH \\ \dot{C}H.OH & \dot{C}H.OH & \dot{C}H.OH \\ \dot{C}OH & \dot{C}H_2.OH & \dot{C}H_2.OH \end{array}$$

I. II. Mannitol and Dulcitol.

But, inasmuch as there are certainly more than two glucoses similar in constitution to sucrodextrose, we are forced to the conclusion that the hypothesis hitherto adopted in explanation of isomerism is insufficient, not only in the case of the alcohols mannitol and dulcitol, but also in the case of the closely related glucoses. We shall have occasion again to discuss their constitution later on.

The first of the above formulæ represents the glucoses as in part *aldehyde* and in part alcohol, whilst according to the second, they are in part *ketone* and in part alcohol, the group COH (formyl) being that which is characteristic of all aldehydes, and the group CO (carbonyl) that which is characteristic of the ketones. The first formula is that which is generally assigned to sucrodextrose and its congeners, and on the whole is more in accordance with the behaviour of the glucoses than the second; but too little is known at present of the glucoses for us to state that all must be represented by it; and even supposing that they are all pentahydric derivatives of normal hexane, which is by no means an established fact, although it is probable that the majority are, it is quite possible that the one formula is applicable to some of them, and that the other is applicable to the remainder.

Inasmuch as cane and milk sugar furnish octacetates when submitted to the action of acetic anhydride in excess, it would appear that the formation of the saccharons from the glucoses is the result of the withdrawal of the elements of a molecule of water from two molecules of glucose in such a manner that each molecule of glucose has one of its hydroxyl groups removed; the relation of the saccharons to the glucoses, supposing the latter to be aldehydic compounds, may therefore be expressed by the following formulæ:

$$C_5H_6(OH)_5.COH \qquad O\left\{\begin{array}{l} C_5H_6(OH)_4.COH \\ C_5H_6(OH)_4.COH \end{array}\right.$$

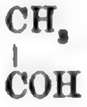
Glucose. Saccharon.

A very large number of isomeric saccharons would appear to be possible, for it is conceivable that the same two glucoses may give rise to a variety of saccharons; but this question cannot at present be usefully discussed. The great difference in the behaviour of the glucoses and of the saccharons, especially cane sugar, with Fehling's solution, seems to afford an argument against the conclusion that the saccharons are also aldehydic compounds as indicated by the above formula; it must be remembered, however, that we have no knowledge of the manner in which Fehling's solution acts as an oxidizing agent, for it is not improbable that its action is quite different from that of ordinary oxidizing agents. Thus, the separation of cuprous oxide may be the result of the decomposition of a cupric derivative of the carbohydrate, and may not be caused by the simple withdrawal of oxygen by the carbohydrate from the cupric salt employed.

The carbohydrates of the composition $(C_6H_{10}O_5)_n$ appear to contain three hydroxyl groups for each six atoms of carbon, since they all furnish triacetates on treatment with acetic anhydride. This fact is of considerable importance, as it enables us to form an idea as to the manner in which the several C_6 groups of which they are composed are 'held together.' The most probable formula which can be assigned to amylin (dextrin) is the following:

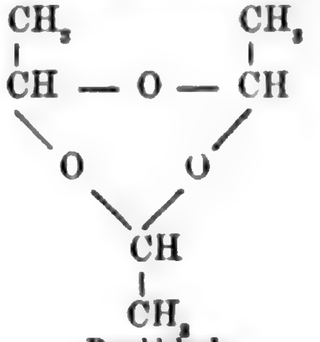
$$O\left\{\begin{matrix} C_5H_6(COH)(OH)_3.O.C_5H_6(COH)(OH)_3 \\ C_5H_6(COH)(OH)_3.O.C_5H_6(COH)(OH)_3 \end{matrix}\right\}O;$$

that is to say, it may be regarded as formed from two molecules of a saccharon, in the same way that the latter is formed from two molecules of a glucose. The formyl groups of the glucose molecules from which it is primarily derived are represented as being still intact, but in the case of the higher members of the group it is not unlikely that the formyl groups also undergo a modification similar to that which we are led to suppose takes place in the conversion of aldehydes,—such as acetic aldehyde,—into polymerides, the nature of which will be understood on reference to the formulæ of acetic aldehyde and of its polymeride, paraldehyde:



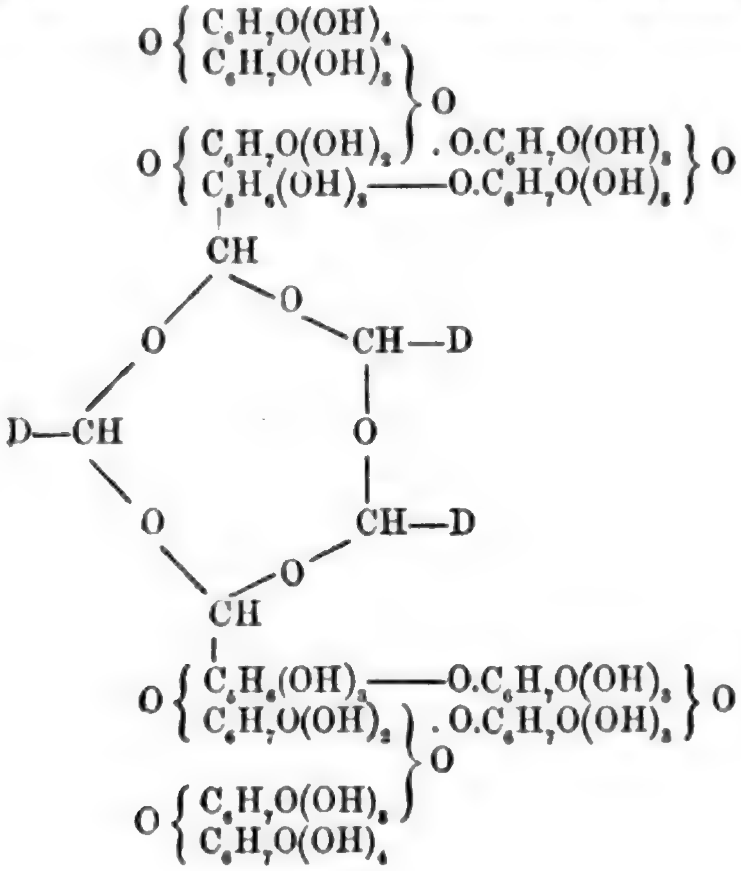
CH_3-COH

Acetic aldehyde.



Paraldehyde.

Starch may be regarded as resulting in this manner from the association of several amylin molecules, and supposing it to have the composition $C_{144}H_{240}O_{120}$ the following formula is that which is most in accordance with its general behaviour:



In this formula the letter D represents a molecule of amylin (dextrin) minus one of its COH groups.

Nomenclature.—Hitherto names have been assigned to the carbohydrates in so arbitrary a manner that they do not afford the slightest indication either of the composition, or of the position in the group, of the bodies to which they refer. But if, as in the case of other groups of compounds, a certain termination be restricted to a certain class of carbohydrates, the name will then afford considerable information with regard to the compound which it designates. Thus it would appear desirable to restrict the termination *ose* exclusively to the *glucoses* or carbohydrates of the composition $C_6H_{12}O_6$; the termination *on* may conveniently be employed for the *saccharons* or carbohydrates of the composition $C_{12}H_{22}O_{11}$, which, like cane sugar, furnish two molecules of glucose on inversion; bodies which, like amylin, furnish a saccharon on hydration may be distinguished by the termination *in;* and terminations such as *en* and *an*, &c., might be employed for the still more complex carbohydrates, such as starch, cellulose, &c. The employment of the vowels in their natural order would thus serve to indicate the position of the carbohydrate in the series; but on account of our imperfect acquaintance with the composition of these bodies, it is obviously desirable to postpone, for the present, the systematization of their names.

§ XIV. THE THIO-ALCOHOLS OR MERCAPTANS.

(1578) These compounds bear the same relation to the alcohols that the metallic hydroxides or hydrates bear to the metallic hydrothionides or sulphydrates; and just as the alcohols may be regarded as derived from water, so the thioalcohols may be regarded as derived from hydrogen sulphide:

$H.OH$	$C_2H_5.OH$	$H.SH$	$C_2H_5.SH$
Water.	Ethylic alcohol.	Hydrogen sulphide.	Thio-ethylic alcohol.

The following are known:

Thioalcohols of the $C_nH_{2n+1}.SH$ *Series.*

	Formula.	M. P. °C.	B. P. °C.
Thiomethylic alcohol	$HS.CH_3$	liquid	21°
Thioethylic „	$HS.C_2H_5$	„	36°
Thiopropylic „	$HS.CH_2.CH_2.CH_3$	„	67°–68°
Thioisopropylic „	$HS.CH(CH_3)_2$	„	57°–60°
Thiobutylic „	$HS.CH_2.CH_2.CH_2.CH_3$	„	97°–98°
Thioisobutylic „	$HS.CH_2CH(CH_3)_2$	„	88°
Thioamylic „	$HS.C_5H_{11}$	„	about 120°

Thioalcohols of the $C_nH_{2n-1}.SH$ *Series.*

Thioallylic alcohol	$HS.CH_2.CH{=}CH_2$	liquid	about 90°

Thioalcohols of the $C_nH_{2n-7}.SH$ *and* $C_nH_{2n-13}.SH$ *Series.*

Thiophenol	$HS.C_6H_5$	liquid	172°·5
Thiobenzylic alcohol	$HS.CH_2.C_6H_5$	„	195°
Thioparacresol	$HS.C_6H_4.CH_3$	43°	188°
Thiometacresol		liquid	—
Thioorthocresol		15°	188°
Thiocarvacrol	$HS.C_6H_3\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$	liquid	236°
Thiothymol		„	234°
Thio-α-naphthol	$HS.C_{10}H_7$	„	—
Thio-β-naphthol		136°	—

Thioalcohols of the $C_nH_{2n}(SH)_2$ *and* $C_nH_{2n-8}(SH)_2$ *Series.*

	Formula.	M. P. ° C.	B. P. ° C.
Thioglycol	$C_2H_4(SH)_2$	liquid	—
Thioresorcinol	$C_6H_4(SH)_2$	27°	245°
Thioquinol		98°	—

Thioalcohols of the $C_nH_{2n-1}(SH)_3$ *Series.*

Thioglycerol	$C_3H_5(SH)_3$	liquid	—

Preparation.—1. By heating together the haloid derivatives of hydrocarbons and potassic sulphydrate in alcoholic solution; thus:

$$\underset{\text{Ethylic chloride.}}{C_2H_5Cl} + KSH = \underset{\text{Thioethylic alcohol.}}{C_2H_5.SH} + KCl.$$

$$\underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} + 2KSH = \underset{\text{Thioglycol.}}{C_2H_4(SH)_2} + 2KCl.$$

This method, however, is not available for the preparation of the thioalcohols corresponding to the phenols. Moreover, it has the objection that the product is always more or less contaminated with the corresponding thioether, the formation of which is explained by the following equations:

$$C_2H_5.SH + KSH = C_2H_5.SK + SH_2;$$
$$C_2H_5.SK + C_2H_5Cl = (C_2H_5)_2S + KCl.$$

2. By distilling a concentrated solution of potassic sulphydrate with the salts formed by neutralizing the acid ethereal sulphates with calcic, potassic or sodic carbonate:

$$\underset{\text{Potassic ethylic sulphate.}}{C_2H_5.KSO_4} + KHS = \underset{\text{Thioethylic alcohol.}}{C_2H_5.SH} + K_2SO_4.$$

3. By distilling the alcohols with phosphoric pentasulphide. According to Carius's researches, however, the formation of thioalcohols in this manner is not the result of the direct displacement of the oxygen of the alcohol by sulphur, but is a consequence of the decomposition of one of the products of the action of the pentasulphide on the alcohol, which takes place in accordance with the equation:

$$5R'.OH + P_2S_5 = 2SH_2 + PSO_3R'_2H + PS_2O_2R'_3.$$

4. By the action of nascent hydrogen (zinc and sulphuric or hydrochloric acid) on the acid chlorides derived from the sulphonic acids; this method has hitherto been employed only for the preparation of thioalcohols corresponding to the phenols, naphthols, and orcinols:

$$\underset{\text{Benzenesulphonic chloride.}}{C_6H_5.SO_2Cl} + 6H = \underset{\text{Thiophenol.}}{C_6H_5.SH} + HCl + 2OH_2.$$

A portion of the chloride is liable, if the temperature rise to 100° (212° F.), to undergo conversion into the sulphonic acid by the action of the water, and thus to escape reduction, as nascent hydrogen is without action on the sulphonic acids; this loss may be avoided, according to Schiller and Otto (*Deut. chem. Ges. Ber.* ix. 1587), by first converting the sulpho-chloride, $R'.SO_2Cl$, into the *sulphinic acid* (q. v.), $R.SO_2H$, and submitting this latter, or one of its salts, to the action of nascent hydrogen.

Properties.—The thioalcohols are mostly colourless or yellow liquids of extremely unpleasant odour, almost insoluble in water. Those corresponding to the monohydric alcohols are bodies of considerable stability, distilling without undergoing any decomposition, but the stability diminishes as the number of SH groups increases. They furnish metallic derivatives with much greater readiness than the alcohols, the hydrogen of the SH group being displaceable not only by the more positive metals, but also by the less positive metals—especially by those which are precipitated as sulphides from acid solutions of their salts by sulphuretted hydrogen. Thus, on shaking their alcoholic solutions with mercuric oxide the corresponding mercury derivative is formed with considerable development of heat, usually separating in the crystalline state; for example:

$$2C_2H_5.SH + HgO = (C_2H_5.S)_2Hg + OH_2.$$

If the undiluted thioalcohol be employed, the action is extremely violent owing to the heat developed. On this account, the thioalcohols have been termed *mercaptans* (from *mercurio aptum*), and their metallic derivatives are often spoken of as *mercaptides*.

On mixing their alcoholic solutions with an alcoholic solution of mercuric chloride, many of the thioalcohols furnish difficultly soluble precipitates of compounds formed by the displacement of the hydrogen of the SH group by the group (HgCl). thioethylic alcohol, for example, yielding a precipitate of the composition $C_2H_5.S(HgCl)$.

These metallic derivatives of the thioalcohols are mostly stable in presence of water; many of them are more or less readily dissolved by hot alcohol, from which they separate in crystals on cooling.

The thioalcohols are also distinguished from the alcohols by their behaviour on oxidation with nitric acid, whereby they are finally converted into *sulphonic acids*; thus:

$$\underset{\text{Thioethylic alcohol.}}{C_2H_5.SH} + 3O = \underset{\text{Ethylsulphonic acid.}}{C_2H_5.SO_3H.}$$

(1579) THIOETHYLIC ALCOHOL; *Ethylic sulphydrate* or *Mercaptan*: $C_2H_5.SH$.—This compound may readily be prepared by the first and second of the methods above described. It is a colourless, very mobile, inflammable liquid, having a most offensive alliaceous odour, of the sp. gr. ·8325 at 21° (69°·8 F.); it boils at 36° (96°·8 F.). It is neutral to vegetable colours, very sparingly soluble in water, but soluble in all proportions in alcohol and ether.

The potassium and sodium derivatives, which may be obtained in the pure state by the action of the metals on the mercaptan, dissolve readily in water, forming alkaline solutions in consequence of their partial decomposition, and they are also decomposed by boiling with alcohol (Claesson, *Journ. pr. Chem.* [2], xv. 193). The metallic derivatives containing the less positive metals are sparingly soluble in water, and are far more stable bodies. The mercury derivative $(C_2H_5.S)_2Hg$, crystallizes in white lustrous scales, which melt at 86° (186°·8 F.). It is not decomposed by an aqueous solution of potassic hydrate, nor by dilute hydrochloric acid, the latter of which dissolves it slowly at the boiling temperature and deposits it again on cooling; it is decomposed, however, by sulphuretted hydrogen in accordance with the equation: $(C_2H_5.S)_2Hg + H_2S = 2C_2H_5.SH + HgS$.

When boiled with moderately strong nitric acid, thioethylic alcohol is ultimately converted into ethylsuphonic acid, $C_2H_5.SO_3H$. According to Friedel and Ladenburg (*Ann. Chem. Pharm.* cxlv. 189), bromine decomposes it in the manner represented by the equation: $2C_2H_5.SH + 3Br_2 = 2C_2H_5Br + S_2Br_2 + 2HBr$. By heating with sulphur to 150° (302° F.), it is converted into the disulphide (Müller, *Journ. pr. Chem.* [2], iv. 39): $2C_2H_5.SH + S = (C_2H_5)_2S_2 + H_2S$.

Potassium and sodium mercaptides are powerful reducing agents, and readily absorb oxygen; in the presence of water or alcohol they are thus converted into the disulphide $(C_2H_5)_2S_2$, but if exposed to air in the dry state they furnish corresponding salts of ethylsulphinic acid, $C_2H_5.SO_2H$ (Claesson).

The thioalcohols homologous with thioethylic alcohol have been very imperfectly investigated. *Thiomethylic* alcohol has been described by Gregory (*Ann. Chem. Pharm.* xv. 239); its mercury derivative crystallizes in shining laminæ, which melt above 100° (212° F.). *Thiopropylic* alcohol has been investigated by Römer (*Deut. chem. Ges. Ber.* vi. 786); its mercury derivative melts at 68° (154°·4 F.). The isomeric *thioisopropylic* alcohol has been described by Claus (*ibid.* v. 659; viii. 532); it is converted into isopropylsulphonic acid by oxidation with nitric acid, but on oxidation with chromic acid it yields a body which is apparently identical with the *duplothioacetone*, $C_6H_{12}S_2$, obtained by the action of trisulphide of phosphorus on acetone. *Thiobutylic alcohol* (*Ann. Chem. Pharm.* clxxi. 251; clxxv. 351), *thioisobutylic* alcohol corresponding to isoprimary butylic alcohol (*ibid.*, xcv. 256), and a mixture of the two *thioamylic* alcohols corresponding to the two fermentation amylic alcohols, are the only other thioalcohols of the $C_nH_{2n+1}.SH$ series hitherto prepared.

Thioallylic alcohol, according to Hofmann and Cahours, closely resembles the thioalcohols of the $C_nH_{2n+1}.SH$ series in its properties.

(1580) THIOPHENOL; *Phenylic sulphydrate* or *Phenylmercaptan*: $C_6H_5.SH$.—This compound is best prepared from benzenesulphonic chloride by Schiller and Otto's method (p. 660). It is obtained also in considerable quantity as one of the products of the destructive distillation of sodic benzenesulphonate, $C_6H_5.SO_3Na$ (Stenhouse, *R. Soc. Proc.* xvii. 62), and by the action of phosphorus sulphide on phenol. Thiophenol is a colourless, highly refractive liquid, having an aromatic, somewhat alliaceous, but by no means offensive odour, if pure; it boils at 172°·5 (341°·6 F.) (Stenhouse). It readily furnishes metallic derivatives; the mercury derivative crystallizes from alcohol in white needles.

Thiophenol is especially characterized by the readiness with which it undergoes conversion into the disulphide $(C_6H_5)_2S_2$. This change even takes place when it is exposed to the air in imperfectly closed vessels (Stenhouse); also when it is gently heated with nitric acid of sp. gr. 1·2, when its solution in alcoholic ammonia is allowed to evaporate spontaneously (Vogt), or when its copper derivate is exposed to the air in a moist state (Stenhouse); when it is submitted to the action of sulphuric acid (Stenhouse), or of sulphuric anhydride (Schiller and Otto); and when its sodium derivative is acted upon by iodine, or chloride or iodide of cyanogen (Hübner and Alsberg; Clemm; Henry). The disulphide is also produced on heating a mixture of thiophenol and benzenesulphinic acid at 100° (212° F.) (Schiller and Otto, *Deut. chem. Ges. Ber.* ix. 1588): $3C_6H_5.SH + C_6H_5.SO_2H = 2(C_6H_5)_2S_2 + 2OH_2$.

Parabromothiophenol, $C_6H_4Br.SH$, obtained by reducing parabromobenzenesulphonic chloride, crystallizes in naphthalene-like plates, which melt at 75° (167° F.); on exposure to the air it slowly oxidizes and is converted into the sulphide $(C_6H_4Br)_2S_2$ (Hübner and Alsberg, *Ann. Chem. Pharm.* clvi. 327).

(1581) THIOBENZYLIC ALCOHOL or *Benzylic sulphydrate*: $C_6H_5.CH_2.SH$, obtained by the action of benzylic chloride on an alcoholic solution of potassic sulphydrate, is a colourless strongly refractive liquid, which greatly irritates the eyes, and has a most unpleasant alliaceous odour; it boils at 194°—195° (381°·2—383° F.). Its mercuric derivative crystallizes from alcohol in long needles. It rapidly oxidizes on exposure to the air, being converted into the disulphide $(C_6H_7CH_2)_2S_2$, which is also formed from it on adding bromine to its ethereal solution (Märcker, *ibid.* cxxxvi. 75; cxl. 86).

The remaining thiophenols closely resemble thiophenol itself in their properties. The *thiocresols* have been described by Märcker (*loc. cit.*), Post and Müller (*ibid.* clxix. 30, 51); *thiocarvacrol* and *thiothymol* by Fittica (*ibid.* clxxii. 325; *Deut. chem Ges. Ber.* vi. 941), Flesch (*ibid.* vi. 478), Roderburg (*ibid.* vi. 669), and Bechler (*Journ. pr. Chem.* [2], viii. 167).

(1582) THIONAPHTHOLS: $C_{10}H_7.SH$.—Maikopar (*Zeits. Chem.* [2], v. 710) has prepared the thionaphthols corresponding to α- and β-naphthol by reducing the chlorides of α- and β-naphthalenesulphonic acids, but they have scarcely been examined.

(1583) THIOGLYCOL: $C_2H_4(SH)_2$.—This compound is obtained by the action of ethylenic chloride on potassic sulphydrate. It is said to be a colourless liquid, which is partially decomposed by distillation. A body intermediate in composition between thioglycol and glycol, and which therefore is represented by the formula $HO.C_2H_4.SH$ has been obtained by Carius (*Ann. Chem. Pharm.*, cxxxiv. 257) by heating the chlorhydrin $C_2H_4Cl.OH$ with an alcoholic solution of potassic sulphydrate. It is a colourless liquid of the consistence of glycol, sparingly soluble in water, having a faint odour like that of thioethylic alcohol; on oxidation with nitric acid it is converted into oxyethylsulphonic or isethionic acid, $C_2H_4(OH).SO_3H$. On boiling its alcoholic solution, sulphuretted hydrogen is evolved, and the analogue of diethylenic alcohol $(C_2H_4.OH)_2S$, is produced.

(1584) THIORESORCINOL and THIOQUINOL: $C_6H_4(SH)_2$.—These compounds are obtained by reducing the chlorides of the corresponding benzene-disulphonic acids (Pazschke, *Journ. pr. Chem.* [2], ii. 418; Körner and Monselise, *Journ. Chem. Soc.*, 1877, i. 80). They are both crystalline substances, and readily yield metallic derivatives; the former has an aromatic odour resembling that of some species of geranium, whilst the latter has an odour distantly resembling that of the *tropæolum*. The colourless crystals of thioquinol become oxidized on exposure to the air, and turn yellow.

(1585) THIOGLYCEROL: $C_3H_5(SH)_3$.—This compound is obtained from the α-trichloropropane formed by displacing the three OH groups in glycerol by chlorine, by heating it with an alcoholic solution of potassic sulphydrate. Compounds intermediate in composition between it and glycerol have been prepared in a similar manner from the chlorhydrins $C_3H_5Cl_2OH$ and $C_3H_5Cl(OH)_2$ (Carius, *Ann. Chem. Pharm.*, cxxii. 72; cxxiv. 222).

These bodies are syrupy liquids of unpleasant odour, soluble in alcohol, very sparingly soluble in water, insoluble in ether. They enter into reaction with metallic oxides and various metallic salts, forming derivatives in which only the hydrogen of the SH groups is displaced by metals. They are decomposed by heat, thioglycerol yielding thioglycide, $C_3H_4S.SH = C_3H_5(SH)_3 - SH_2$; while more complex products are obtained from those containing less sulphur, owing to their losing the elements both of water and sulphuretted hydrogen. Their behaviour on oxidation appears to be similar to that of other thioalcohols.

CHAPTER VII.

THE ETHERS.

§ I. *The Ethers*; — § II. *The Ether-Alcohols*; — § III. *The Glucosides*; — § IV. *The Thioethers, Selenides and Tellurides.*

THE ethers are the anhydrides of the alcohols, to which they bear the same relation that the metallic oxides, such as sodic and calcic oxide, bear to the corresponding hydroxides or hydrates; thus:

$Na.OH$	$Na.O.Na$	$C_2H_5.OH$	$C_2H_5.O.C_2H_5$
Sodic hydroxide.	Sodic oxide.	Ethylic alcohol.	Ethylic ether.
$Ca(OH)_2$	CaO	$C_2H_4(OH)_2$	C_2H_4O
Calcic hydroxide.	Calcic oxide.	Ethylenic alcohol.	Ethylenic oxide.

Preparation.—1. The ethers corresponding to the monohydric alcohols are obtained by the action of the monohaloid derivatives of the hydrocarbons on the potassium or sodium derivatives of the alcohols; for example:

$$\underset{\text{Sodium ethoxide.}}{C_2H_5.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl ether.}}{C_2H_5.O.C_2H_5} + NaI.$$

If the metallic derivative of the alcohol and the haloid hydrocarbon derivative contain the same radicle, as is the case in the example here quoted, so-called *simple ethers* are formed; but if the radicles are isomeric, homologous, or isologous, *mixed ethers* result, the formation of several of which is illustrated by the following equations:

$$C_3H_7{}^{\alpha}.ONa + C_3H_7{}^{\beta}I = C_3H_7{}^{\alpha}.O.C_3H_7{}^{\beta} + NaI.$$
$$C_2H_5.ONa + CH_3I = CH_3.O.C_2H_5 + NaI.$$
$$C_6H_5.ONa + CH_3I = C_6H_5.O.CH_3.$$

The preparation of the homologues of ethyl ether (and probably of the higher ethers of other series) by this method becomes more and more difficult as the series is ascended, on account of the conversion of the monohaloid paraffin into the corresponding olefine under the influence of the metallic derivative of the alcohol; the tendency to undergo this decomposition not only increases as the series is ascended, but is also greater in the case of the tertiary than in the case of the secondary or primary derivatives: hence the ethers corresponding to the primary alcohols are more readily prepared than those which correspond to the secondary, and the secondary more readily than the tertiary. Moreover, only those haloid derivatives can be made use of which are without difficulty convertible into alcohols: compounds such as bromobenzene, for example, which do not yield up the halogen in exchange for other radicles under any ordinary treatment, being without action on the metallic derivatives of the alcohols; while others, such as the chloropropylenes from propylenic chloride (1243), lose the elements of a molecule of hydrochloric acid.

2. A second method, which is available for the preparation of simple and mixed ethers corresponding to the alcohols of the ethylic and allylic series, consists in distilling the acid ethereal salts formed from these alcohols and sulphuric acid with the alcohols themselves:

$$\underset{\text{Acid ethereal sulphate.}}{R'.HSO_4} + \underset{\text{Alcohol.}}{R'.OH} = \underset{\text{Ether.}}{R'.O.R'} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$
$$C_2H_5.HSO_4 + C_2H_5.OH = C_2H_5.O.C_2H_5 + H_2SO_4.$$
$$C_2H_5.HSO_4 + C_5H_{11}.OH = C_2H_5.O.C_5H_{11} + H_2SO_4.$$

3. Simple and mixed ethers corresponding to the alcohols of the ethylic and allylic series are also formed on heating the corresponding haloid hydrocarbon derivatives with argentic or mercuric oxide:

$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI.$$

4. Little is known of the simple ethers of the polyhydric alcohols. Those corresponding to the dihydric alcohols are pre-

pared by withdrawing the elements of a molecule of hydrochloric acid from their chlorhydrins:

$$\underset{\text{Glycol chlorhydrin.}}{C_2H_4Cl.OH} + KHO = \underset{\text{Ethylenic oxide.}}{C_2H_4O} + KCl + OH_2.$$

Mixed ethers derived from polyhydric and monohydric alcohols are readily obtained by the action of monohaloid hydrocarbon derivatives on the sodium derivatives of the former; thus:

$$C_2H_4(ONa)_2 + 2C_2H_5I = C_2H_4(OC_2H_5)_2 + 2NaI.$$

Properties.—The ethers derived from monohydric alcohols are, with few exceptions, colourless liquids, having an agreeable odour, sparingly soluble, or insoluble in water, and boiling at a lower temperature than the metameric alcohols. In chemical behaviour there is a considerable difference between the simple and mixed ethers derived from the carbinols—or alcohols which may be regarded as formed from carbinol, $CH_3.OH$, by the displacement of one or more of the three atoms of hydrogen in the CH_3 group by hydrocarbon radicles—and the mixed ethers, such as methylphenyl ether, $CH_3.O.C_6H_5$, derived from the phenols and carbinols. The former are slowly decomposed when heated with water, and reconverted into alcohols:

$$C_2H_5.O.C_2H_5 + OH_2 = 2C_2H_5.OH.$$

On digestion with concentrated sulphuric acid, they yield the corresponding acid ethereal sulphates:

$$(C_2H_5)_2O + H_2SO_4 = C_2H_5.HSO_4 + C_2H_5.OH;$$
$$C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + OH_2.$$

When submitted to the action of the haloid phosphorus compounds they are converted into haloid hydrocarbon derivatives:

$$C_2H_5.O.C_2H_5 + PCl_5 = 2C_2H_5Cl + POCl_3.$$

The ethers, however, are much less readily acted upon by the haloid phosphorus compounds than the alcohols. They are also converted into haloid hydrocarbon derivatives by the action of the haloid acids, hydriodic acid decomposing them most readily; thus:

$$(C_2H_5)_2O + HI = C_2H_5I + C_2H_5.OH.$$

Silva has shown (*Compt. Rend.* lxxxi. 323), that when the mixed ethers of the $C_nH_{2n+1}.O.C_mH_{2m+1}$ series are decomposed by saturating them with hydriodic acid gas in the cold, the radicle containing the fewest carbon atoms is separated as iodide, ethyl methyl ether, for example, being almost entirely broken up in accordance with the equation :

$$CH_3.O.C_2H_5 + HI = CH_3I + C_2H_5.OH.$$

On the other hand, the mixed ethers formed from the phenols by displacing the hydrogen of the OH group by radicles derived from the hydrocarbons of the paraffin or olefine series are scarcely, if at all, altered by heating with water. They furnish haloid substitution derivatives when submitted to the action of the haloid phosphorus compounds :

$$C_6H_5.O.CH_3 + PCl_5 = C_6H_4Cl.O.CH_3 + HCl + PCl_3.$$

They are converted into sulphonic acids by the action of sulphuric acid :

$$C_6H_5.O.CH_3 + H_2SO_4 = C_6H_4(HSO_3).O.CH_3 + OH_2.$$

And they are decomposed by the haloid acids, although much less readily than the ethers derived solely from the carbinols, in the manner represented by the equation :

$$C_6H_5.O.CH_3 + HI = C_6H_5.OH + CH_3I.$$

Both classes of ethers are oxidized with difficulty, especially those derived from the phenols ; but when oxidized, they furnish essentially the same products as the alcohols from which they are derived.

The ethers corresponding to the dihydric alcohols, to judge from the behaviour of those derived from the glycols, are far less inert compounds than those formed from monohydric alcohols. Thus, ethylenic oxide readily combines with water and the haloid acids in the manner expressed by the equations :

$$C_2H_4O + OH_2 = C_2H_4(OH)_2$$
$$C_2H_4O + HCl = C_2H_4Cl.OH.$$

The following ethers derived from monohydric alcohols are known :

Ethers of the $C_nH_{2n+1}.O.C_mH_{2m+1}$ *Series.*

		M. P.	B. P. °C.
Methyl ether	$CH_3.O.CH_3$	—	−21°
Methyl ethyl ether	$CH_3.O.C_2H_5$	—	+11°
Ethyl ether	$C_2H_5.O.C_2H_5$	—	35°·5
Methyl propyl ether	$CH_3.O.C_3H_7{}^{\alpha}$	—	49°–52°
Ethyl propyl ether	$C_2H_5.O.C_3H_7{}^{\alpha}$	—	68°–70°
Propyl ether	$C_3H_7{}^{\alpha}.O.C_3H_7{}^{\alpha}$	—	86°
Isopropyl ether	$C_3H_7{}^{\beta}.O.C_3H_7{}^{\beta}$	—	60°
Ethyl butyl ether	$C_2H_5.O.C_4H_9{}^{\alpha}$	—	91°·7

		M. P.	B. P. ° C.
Ethyl isobutyl ether*	$C_2H_5.O.C_4H_9^{\beta}$	—	78°–80°
Methyl isoamyl ether*	$CH_3.O.C_5H_{11}$	—	92°
Ethyl isoamyl ether	$C_2H_5.O.C_5H_{11}^{\alpha}$	—	112°
Butyl ether	$C_4H_9^{\alpha}.O.C_4H_9^{\alpha}$	—	140°·5
Isobutyl ether	$C_4H_9^{\beta}.O.C_4H_9^{\beta}$	—	110°
Propyl isoamyl ether	$C_3H_7^{\alpha}.O.C_5H_{11}$	—	125°–130°
Isoamyl ether	$C_5H_{11}.O.C_5H_{11}$	—	176°
Ethyl cetyl ether	$C_2H_5.O.C_{16}H_{33}$	20°	—
Isoamyl cetyl ether	$C_5H_{11}.O.C_{16}H_{33}$	30°	—
Cetyl ether	$C_{16}H_{33}.O.C_{16}H_{33}$	55°	about 300°

Ethers of the $(C_nH_{2n-1})_2O$ *and* $C_nH_{n-1}.O.C_nH_{2n+1}$ *Series.*

		M. P.	B. P. ° C.
Allyl ether	$C_3H_5.O.C_3H_5$	—	85°–87°
Allyl methyl ether	$C_3H_5.O.CH_3$	—	46°
Allyl ethyl ether	$C_3H_5.O.C_2H_5$	—	64°
Allyl isoamyl ether	$C_3H_5.O.C_5H_{11}$	—	120°
Isocrotyl methyl ether	$(CH_3)_2C{=}CH.OCH_3$	—	70°–74°
Isocrotyl ethyl ether	$(CH_3)_2C{=}CH.OC_2H_5$	—	92°–94°

Ethers of the $C_nH_{2n-3}.O.C_nH_{2n+1}$ *Series.*

		M. P.	B. P. ° C.
Propargyl methyl ether	$C_3H_3.O.CH_3$	—	61°–62°
Propargyl ethyl ether	$C_3H_3.O.C_2H_5$	—	81°–85°
Propargyl isoamyl ether	$C_3H_3.O.C_5H_{11}$	—	140°–145°

Ethers of the $(C_nH_{2n-7})_2O$ *and* $C_nH_{2n-7}.O.C_nH_{2n+1}$ *Series.*

		M. P.	B. P. ° C.
Phenyl ether	$C_6H_5.O.C_6H_5$	28°	248°
Phenyl benzyl ether	$C_6H_5.O.CH_2.C_6H_5$	39°	287°
Phenyl methyl ether	$C_6H_5.O.CH_3$	liquid	152°
Phenyl ethyl ether	$C_6H_5.O.C_2H_5$	"	172°
Phenyl isoamyl ether	$C_6H_5.O.C_5H_{11}$	"	225°
Phenyl allyl ether	$C_6H_5.O.C_3H_5$	"	192°–195°
Orthocresyl methyl ether	$CH_3.C_6H_4.O.CH_3$	"	174°
Metacresyl " "		"	175°–176°
Paracresyl " "		"	174°
Metacresyl ethyl "	$CH_3.C_6H_4.O.C_2H_5$	"	191°
Paracresyl " "		"	188°
Benzyl methyl ether	$C_6H_5.CH_2.O.CH_3$	"	168°
Benzyl ethyl ether	$C_6H_5.CH_2.O.C_2H_5$	"	185°
Thymyl methyl ether	$\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}C_6H_3.O.CH_3$	"	216°·7
Cymenyl " "		"	216°·8
Thymyl ethyl ether	$C_{10}H_{13}.O.C_2H_5$	—	222°
Allylphenyl methyl ether (anethol)	$C_3H_5.C_6H_4.O.CH_3$	21°	232°

Ethers of the $C_nH_{2n-13}.O.C_nH_{2n+1}$ *Series.*

		M. P.	B. P. ° C.
α-Naphthyl ethyl ether	$C_{10}H_7.O.C_2H_5$	liquid	280°·7
β-Naphthyl " "		33°	—

(1586) **Methylic oxide or ether**: $CH_3.O.CH_3$.—To prepare this ether, a mixture of 1·3 pts. methylic alcohol and 2 pts. concentrated sulphuric acid is gradually heated in a flask attached to a reversed condenser to 140° (284° F.); gas begins to be regularly evolved at 110° (230° F.), and is passed through sodic hydrate solution to free it from sulphurous anhydride, and then into sulphuric acid which is cooled by water. The acid dissolves about 600 times its volume of the gas, probably forming the compound $SO(OH)_2(OCH_3)_2$; the solution may be preserved for any length of time, and the ether liberated when required by allowing it to drop into water (Erlenmeyer and Kriechbaumer, *Deut. chem. Ges. Ber.*, vii. 699).

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* The isobutyl and isoamyl ethers have all been prepared from the fermentation alcohols: the latter are therefore mixtures.

Methylic ether is a colourless gas of pleasant ethereal odour, which may be condensed by a refrigerating mixture of ice and salt, or by pressure, to a liquid boiling at about – 21° (– 5°·8 F.). On account of its volatility, it is employed in the artificial production of ice. Water at 18° (64°·4 F.) dissolves 37 times its volume of the gas. When it is passed, together with hydrochloric acid, through well-cooled tubes, a liquid condenses which varies somewhat in composition according to the pressure under which it is produced, but apparently consists of the compound $C_2H_6O.HCl$ with more or less of the ether or of hydrochloric acid dissolved in it according to circumstances; it boils at – 1° (29°·8 F.), but is in great part dissociated (Friedel, *Compt. Rend.* lxxxi. 152, 236).

It combines with sulphuric anhydride, forming methylic sulphate $(CH_3)_2SO_4$. When submitted to the action of chlorine in sunlight, it furnishes chlorinated derivatives. The monochloro-derivative, $CH_3.O.CH_2Cl$, boils at 59°·7 (139°·5 F.); it is dissolved by water and decomposed into hydrochloric acid, methylic alcohol, and so-called trioxymethylene—the polymeride of formic aldehyde; ammonia converts it into hexamethylenamine; and it readily acts on dry potassic acetate forming the compound $CH_3.O.CH_2(C_2H_3O_2)$ (Friedel, *ibid.* lxxxiv. 247). The dichlorinated derivative, $CH_2Cl.O.CH_2Cl$, boils at 105° (221° F.), and, when decomposed by water, yields hydrochloric acid, and the polymeride of formic aldehyde.

(1587) ETHYLIC OXIDE OR ETHER; *Ether; Sulphuric Ether:* $C_2H_5.O.C_2H_5$.—Ethylic ether may be formed in a variety of ways, but on the large scale it is always prepared from ethylic alcohol by the so-called continuous process of Boullay.

A mixture of 5 pts. 90 per cent. alcohol and 9 pts. concentrated sulphuric acid is heated to a temperature of 140°—145° (284°—293° F.) in a vessel provided with an efficient condenser, and a constant stream of alcohol is allowed to flow in at such a rate that the temperature of the mixture is maintained at about 140° (284° F.). The liquid which passes over consists almost entirely of ether and water, mixed with a small portion of alcohol which has distilled over unchanged; the quantity of alcohol which thus escapes etherification depending upon the rapidity with which the operation is conducted, being greater the more quickly it is performed. The other impurities are sulphurous anhydride, acetic acid, and a little so-called oil of wine, which is a mixture of ethylic sulphate, $(C_2H_5)_2SO_4$, and hydrocarbons polymeric with ethylene.

In order to purify the ether, it is agitated with an equal volume of milk of lime, and is then rectified from the water bath. But it still retains alcohol after being thus treated; this may be in great part removed by agitating it repeatedly with water, after which it may be dried or rendered *absolute* by means of quicklime or fused calcic chloride, and then rectified. The last traces of alcohol, however, can only be removed by allowing the dry ether to remain for a considerable time in contact with metallic sodium, and then distilling it from the water bath, or by distilling it several times from sodium.

The formation of ether in this manner is generally regarded as the result of two distinct changes, the first of which consists in the production of ethylic hydric sulphate:

$$C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + OH_2;$$

which then enters into reaction with a further portion of alcohol to form ethylic ether and sulphuric acid:

$$C_2H_5.HSO_4 + C_2H_5.OH = (C_2H_5)_2O + H_2SO_4.$$

The sulphuric acid thus liberated is again converted into ethylic hydric sulphate, which is in turn decomposed by the alcohol, and this cycle of changes is repeated over and over again. Theoretically, therefore, the same quantity of acid should suffice to convert an unlimited amount of alcohol into ether, but practically this is not the case, chiefly because oxidation and carbonization take place at the expense of the acid, 1 pt. of acid being capable of converting only about 5 pts. of alcohol into ether. If the temperature be allowed to rise above about 145° (293° F.), the ethylic hydric sulphate undergoes decomposition into ethylene and sulphuric acid, and below about 140° (284° F.), the etherification of the alcohol takes place very slowly, for although ether may be formed by heating ethylic hydric sulphate with alcohol at 100° (212° F.), it is only at about 140° (293° F.) that the change is rapidly effected; moreover, if the temperature be not considerably above 100° (212° F.), the water produced in the reaction does not distil over, and the acid becomes too weak to effect the etherification.

The most conclusive proof of the correctness of this explanation is afforded by Williamson's observation that if a mixture of (fermentation) amylic alcohol and sulphuric acid—*i.e.*, amylic hydric sulphate, be submitted to distillation with ethylic alcohol, the mixed ether, isoamyl methyl ether, is produced, the residue in the retort when only ethylic ether passes over consisting of ethylic hydric sulphate; thus:

$$C_5H_{11}.OH + H_2SO_4 = C_5H_{11}.HSO_4 + OH_2;$$
$$C_5H_{11}.HSO_4 + C_2H_5.OH = C_5H_{11}.O.C_2H_5 + H_2SO_4.$$

Ether is also produced on distilling ethylic sulphate with alcohol (Erlenmeyer), and it is possible therefore that the following reactions play a part in the formation of ether by the continuous process:

$$2C_2H_5.OH + H_2SO_4 = (C_2H_5)_2SO_4 + 2OH_2;$$
$$(C_2H_5)_2SO_4 + C_2H_5.OH = (C_2H_5)_2O + C_2H_5.HSO_4.$$
$$(C_2H_5)_2SO_4 + 2C_2H_5.OH = 2(C_2H_5)_2O + H_2SO_4.$$

Other methods of converting alcohol into ether are by heating it under pressure with sulphuric acid diluted with water (Reynoso, *Ann. Chem. Phys.* [3], xlviii. 435; Erlenmeyer, *Ann. Chem. Pharm.* clxii. 373), with the haloid acids, or with the monohaloid derivatives of ethane; for example:

$$C_2H_5.OH + HCl = C_2H_5Cl + OH_2;$$
$$C_2H_5.OH + C_2H_5Cl = (C_2H_5)_2O + HCl.$$

Various salts are also capable of etherifying alcohol, apparently without undergoing change themselves. Thus Reynoso has found that ether is produced in considerable quantity on heating alcohol at 240° (464° F.) in sealed tubes with the sulphates isomeric with magnesic sulphate, or with the chlorides of cadmium, cobalt, copper, and manganese, or with bromide or iodide of cadmium. If normal aluminic sulphate be employed, the etherification takes place between 200° and 240° (392° and 464° F.), without liberation of gas, and with but little formation of basic sulphate; when alum is used the results are similar, but the alcohol is etherified at a lower temperature. Aluminic, ferric, and zincic chlorides furnish a mixture of ether and monochlorethane. There can be little doubt that in most of these cases the etherification is due to the action of a small amount of acid formed by the decomposition of a portion of the salt employed; in others perhaps it is at least partially the result of successive changes such as are represented by the following equation:

$$ZnCl_2 + C_2H_5.OH = ZnCl.OC_2H_5 + HCl.$$
$$ZnCl.OC_2H_5 + C_2H_5.OH = ZnCl.OH + (C_2H_5)_2O.$$

In all these cases, however, the alcohol is never completely converted into ether in consequence of the occurrence of changes which are the reverse of those by which the ether is formed. For example, when monochlorethane is heated with alcohol, not only is ether produced, but the hydrochloric acid which is the accessory product reacts more or less upon the ether and reconverts it into alcohol and monochlorethane; thus:

$$C_2H_5.OH + C_2H_5Cl = HCl + (C_2H_5)_2O;$$
$$(C_2H_5)_2O + HCl = C_2H_5.OH + C_2H_5Cl.$$

The extent to which changes of this kind occur depends chiefly upon the relative amounts of the different substances present, and on the temperature to which the mixture is heated.

Ethylic ether is a colourless, transparent, very mobile liquid, having a peculiar exhilarating odour and sharp, burning taste, with cooling after taste. It boils at 35°·6 (96° F.), and at 0° (32° F.) has the sp. gr. ·736. Dry ether does not solidify, even in a mixture of carbonic anhydride and ether (Franchimont). It is very inflammable, and its vapour detonates with great violence when mixed with air and ignited. It dissolves in about 9 pts. of water at ordinary temperatures, and itself dissolves about one-eleventh of its weight of water; it is miscible in all proportions with anhydrous methylic and ethylic alcohols, and with many other liquids. It readily dissolves most highly hydrogenized carbon compounds, which are sparingly soluble in alcohol, such as fats and resins, but is very seldom a good solvent for substances which are easily soluble in alcohol.

Ether also dissolves bromine and iodine, and many metallic bromides and chlorides in considerable quantity. The solution of these substances by ether is apparently connected with the fact that they form compounds with it. Thus, on mixing together bromine and ether in a vessel surrounded by a refrigerating mixture of ice and salt, a red crystalline body of the composition $(C_4H_{10}O)_2Br_6$ is obtained, which melts at 22° (71°·6 F.) and does not give off bromine under the ordinary pressure, but gradually undergoes spontaneous decomposition and becomes liquid when kept; it is instantly resolved by water into its generators (Schützenberger, *Compt. Rend.* lxxv. 1511). In a similar manner, crystalline compounds of ether with stannic chloride, $2C_4H_{10}O.SnCl_4$, with titanic chloride, $C_4H_{10}O.TiCl_4$, and vanadic oxychloride, $VOCl_3.C_4H_{10}O$ (Bedson, *Journ. Chem. Soc.* 1876, i. 309), with antimonic chloride, $SbCl_5.C_4H_{10}O$ (Carleton Williams, *ibid.*, ii. 463), and with many other chlorides, &c. (comp. Nicklès, *Compt. Rend.*, lii. 396; lviii. 537; lx. 479, 800), may be obtained by mixing the chlorides with ether, taking care to prevent rise of temperature. They are all decomposed by water, and decompose either spontaneously when kept, or on heating; the titanium compound, $C_4H_{10}O.TiCl_4$, for example, when heated, is converted into the chlorethylin $TiCl_3.OC_2H_5$ and chlorethane. The stannic chloride compound, however, is said to volatilize unchanged.

Ether burns with a much more luminous flame than alcohol, and soot is deposited on cold bodies introduced into the flame. If burned with insufficient air, by passing the vapour mixed with air over platinum black for example, it yields a mixture of aldehyde with acetic acid and acetal. It also gradually absorbs oxygen on exposure to the air; according to Kingzett (*Year Book of Pharmacy*, 1876, 554), hydric peroxide and perhaps ethylic acetate are produced by its atmospheric oxidation. With other oxidizing agents, it yields products similar to those obtained under analogous conditions from alcohol, but is much less readily acted upon than the latter; thus, when heated with nitric acid, it furnishes carbonic anhydride, and acetic and oxalic acids.

It is slowly decomposed in contact with water, even at ordinary atmospheric temperatures, and much more rapidly when heated with it, being converted into alcohol; this change is facilitated by acids, but not by alkalies. In contact with sodic chloride, calcic chloride, or anhydrous cupric sulphate, it is slowly decomposed, acquiring the property of giving the iodoform reaction, which is not the case with ether which has been many months in contact with potassic hydrate or carbonate; this is perhaps due to the formation of an ethylate, thus:

$$CuSO_4 + (C_2H_5)_2O = C_2H_5O.SO_2.O.Cu.OC_2H_5.$$

(Lieben, *Ann. Chem. Pharm.*, clxv. 134). Potassium and sodium are without action on pure ether. It combines with sulphuric anhydride, forming ethylic sulphate, $(C_2H_5)_2SO_4$; and when warmed with concentrated sulphuric acid, it yields hydric ethylic sulphate.

(1588) ***Chlorinated Derivatives of Ethylic Ether.***—Chlorine acts very readily, even at temperatures below 0° (32° F.), on ether, converting it in the first instance into monochlorinated ether, from which, by the continued action of chlorine in diffused light, di-, tri-, tetra- and pentachlorether are formed; and by the prolonged action of chlorine assisted by sunlight, the perchlorinated compound $C_4Cl_{10}O$ is finally produced.

Monochlorether, $C_2H_5.O.CHCl.CH_3$, is the first product of the action of chlorine on carefully cooled ether; it may also be obtained by saturating a mixture of aldehyde with twice its volume of anhydrous alcohol with hydrochloric acid gas, its formation in the latter case being represented by the equations:

$$CH_3.COH + HCl = CH_3.CHCl.OH;$$
$$CH_3.CHCl.OH + C_2H_5.OH = CH_3.CHCl.O.C_2H_5 + HCl.$$

It is a colourless liquid, boiling with slight decomposition at 97°—98° (206°·6—208°·4 F.). Concentrated sulphuric acid decomposes it with formation of aldehyde, ethylic hydric sulphate, and hydrochloric acid (Jacobsen, *Deut. chem. Ges. Ber.*, iv. 215):

$$CH_3.CHCl.O.C_2H_5 + H_2SO_4 = C_2H_5.HSO_4 + CH_3.COH + HCl.$$

Dichlorether, $C_2H_5.O.CHCl.CH_2Cl$, is the chief product of the action of chlorine on ether at temperatures not exceeding 20°—30° (68°—86° F.) (Lieben, *Ann. Chem. Pharm.*, cxlvi. 180; clxxviii. 29; Abeljanz, *ibid.*, clxiv. 197; Jacobsen, *loc. cit.*). It is best prepared by passing chlorine into ether cooled to 0° (32° F.), and after some time distilling the product in the water bath; the distillate is again submitted to the action of chlorine, and the product distilled, and this treatment repeated until the amount volatile below 100° (212° F.) becomes very small. The residues are then distilled until the boiling point reaches 136° (276°·8 F.), the distillate is treated with chlorine, and finally, after another repetition of this treatment, the entire product not volatile below 136° (276°·8 F.) is submitted to fractional distillation.

It is a limpid, colourless liquid, boiling with slight decomposition at about 145° (293° F.). Like monochlorether it is slowly decomposed by water at ordinary temperatures, and more rapidly on heating, yielding a mixture of the monethylin of monochloraldehydrol, $CH_2Cl.CH(OH).OC_2H_5$, which boils at 95° — 96° (203° — 204°·8 F.), with the condensation product $[CH_2Cl.CH(OC_2H_5)]_2O$, which boils at about 165° (329° F.). On treatment with concentrated sulphuric acid it furnishes monochloraldehyde, hydric ethylic sulphate, and hydrochloric acid:

$$CH_2Cl.CHCl.OC_2H_5 + H_2SO_4 = CH_2Cl.COH + C_2H_5.HSO_4 + HCl.$$

By the action of sodic ethylate it is converted into monochloracetal, $CH_2Cl.CH(OC_2H_5)_2$. Phosphoric pentachloride acts upon it chiefly in the manner represented by the equation:

$$CH_2Cl.CHCl.OC_2H_5 + PCl_5 = CH_2Cl.CHCl_2 + C_2H_5Cl + POCl_3.$$

An isomeric dichlorether, $CH_3.CHCl.O.CHCl.CH_3$, is formed on saturating anhydrous aldehyde cooled to 0° (32° F.) with hydrochloric acid gas:

$$CH_3.COH + HCl = CH_3.CHCl(OH);$$
$$CH_3.CHCl(OH) + CH_3.CHCl(OH) = CH_3.CHCl.O.CHCl.CH_3 + OH_2.$$

It is a colourless, limpid liquid, boiling at about 116° (240°·8 F.); it is much more easily decomposed by water than the isomeric compound, being converted into aldehyde and hydrochloric acid (Lieben, *Ann. Chem. Pharm.*, clxxviii. 43).

The dichlorethers readily exchange their chlorine for hydrocarbon radicles when submitted to the action of the zinc organo-metallic compounds (comp. pp. 411, 452).

Trichlorether, $CHCl_2.CHCl.OC_2H_5$.—In order to convert dichlorether into the higher chlorinated derivatives, the action of chlorine requires to be assisted by heat; the tri-, tetra-, and pentachlorinated compounds have not been isolated from the product in the pure state, however, as they partially decompose on distillation, although their presence may be indirectly proved by the action of sodic ethylate and of sulphuric acid on the product. Thus when the residue boiling above 155° (311° F.) obtained in the preparation of dichlorether is submitted to the action of sodic ethylate, a product is obtained from which dichloracetal, $CHCl_2.OH(OC_2H_5)_2$, may be separated by fractional distillation, proving the presence of a trichlorether of the formula $CHCl_2.CHCl.OC_2H_5$ (Jacobsen).

Similarly, the product obtained by carrying on the action of chlorine for some time at about 90° (194° F.), when treated with concentrated sulphuric acid, yields a considerable quantity of chloral, $CCl_3.COH$, and therefore contains the *tetrachlorether* $CCl_3.CHCl.OC_2H_5$ (Jacobsen). This ether may be obtained in the pure state by the action of phosphoric pentachloride on the monethylin of trichloraldehydrol (Henry, *Deut. chem. Ges. Ber.*, iv. 101):

$$CCl_3.CH(OH).OC_2H_5 + PCl_5 = CCl_3.CHCl.OC_2H_5 + HCl + POCl_3.$$

It boils at 190° (374° F.); by heating with alcohol, it is converted into trichloracetal, $CCl_3.CH(OC_2H_5)_2$, and also furnishes this compound when acted upon by sodic ethylate or by a very strong alcoholic solution of potassic hydrate, but a 10 per cent. solution of potassic hydrate apparently converts it into the compound $CCl_2{=}CCl.OC_2H_5$ (Wurtz and Vogt, *Compt. Rend.*, lxxiv. 777; Paterno and Pisati, *Gaz. chim. ital.*, ii. 333).

The end product of the action of chlorine in diffused light, assisted by heat, is the *pentachlorether*, $CCl_3.CCl_2.OC_2H_5$. Hence it appears that the action of chlorine on ether in diffused light is restricted to the one ethyl group, and that the order in which the hydrogen atoms are displaced may be represented by the formula $CH_3.CH_2.OC_2H_5$ (Jacobsen); the crude mixture of higher chlorinated derivatives
2·3·4·1·5
has not yet been sufficiently investigated, however, to enable us to state that displacement takes place only in this order (comp. Henry, *Deut. chem. Ges. Ber.*, vii. 763).

An isomeric pentachlorether, $CCl_3.CHCl.O.CH_2.CH_2Cl$, may be obtained by the action of phosphoric pentachloride on the compound $CCl_3.CH(OH).O.CH_2.CH_2Cl$, formed by the union of chloral with the chlorhydrin of glycol, $CH_2(OH).CH_2Cl$; it boils without change at 235° (455° F.) (Henry, *loc. cit.*)

Perchlorethylic ether, $C_4Cl_{10}O$, the end product of the prolonged action of chlorine on ether in sunshine, according to Regnault, by whom it was discovered in 1830, is a crystalline substance which melts at 69° (156°·2 F.); it boils at about 300° (572° F.), but is at the same time resolved into hexachlorethane and trichloracetic chloride: $(C_2Cl_5)_2O = C_2Cl_6 + CCl_3.COCl$.

The remaining homologues of ethylic ether, which have mostly either been prepared by the action of sulphuric acid on the corresponding alcohols, or by heating monohaloid derivatives of paraffins with the sodium derivatives of the alcohols of the ethylic series, manifest the closest resemblance in their properties to ethylic ether.

(1589) ETHERS OF THE $(C_nH_{2n-1})_2O$ AND $C_nH_{2n+1}.O.C_nH_{2n-1}$ SERIES.—These ethers are prepared by methods precisely similar to those employed in the preparation of the ethers of the ethylic series, and they appear to bear the same relation in properties to these latter, that allylic alcohol bears to ethylic alcohol. According to Eltekoff's recent experiments, however (*Deut. chem. Ges. Ber.*, x. 704), the behaviour of the ethers of the form $(C_nH_{2n+1})_2C{=}CH.OC_nH_{2n+1}$, when heated with dilute sulphuric acid, is somewhat peculiar, isocrotyl ethyl ether (p. 396), $(CH_3)_2C{=}CH.OC_2H_5$, being apparently thereby converted into isobutyric aldehyde, $(CH_3)_2CH.COH$, and ethylic alcohol.

(1590) ETHERS OF THE $C_nH_{2n+1}.O.C_nH_{2n-3}$ SERIES.—The ethers of this series are obtained from the corresponding terms of the $C_nH_{2n+1}.O.C_nH_{2n-1}$ series by combining them with bromine, and submitting the bromides obtained to the action of an alkali. For example, ethyl allyl ether, $C_2H_5.O.C_3H_5$, unites directly with bromine, forming the dibromide $C_2H_5.O.C_3H_5Br_2$, and on distilling this compound in the oil bath from pieces of solid sodic hydrate, ethyl monobromallyl ether, $C_2H_5.O.C_3H_4Br$, is produced. This is a colourless liquid of pleasant odour, boiling at 130°—135° (266°—275° F.); by heating with a very concentrated alcoholic solution of potassic hydrate, it is readily converted into ethyl propargyl ether, $C_2H_5.O.C_3H_3$ (Henry, *Deut. chem. Ges. Ber.*, v. 188; 274). This ether is also formed by the action of an alcoholic solution of potassic hydrate on α-tribromopropane (tribromohydrin), and several other chloro- and bromo-derivatives of propane and propylene (comp. Liebermann and Kretschmer, *Ann. Chem. Pharm.*, clviii. 230). It is a mobile liquid of penetrating odour, lighter than water, boiling slightly above 80° (176° F.); it combines with bromine to form the compound $C_3H_3Br_2.O.C_2H_5$, which is reconverted into the ether by the action of sodium amalgam on its alcoholic solution. It also exhibits the property, which is apparently characteristic of all propargyl compounds, that of forming metallic derivatives. Thus, on adding a concentrated solution of argentic nitrate to its alcoholic solution, a crystalline precipitate is obtained having the composition $(C_3H_2Ag.OC_2H_5)_2,AgNO_3$, which on treatment with ammonia is converted into an amorphous silver derivative of the composition $C_3H_2Ag.OC_2H_5$. A corresponding cuprous derivative, $(C_3H_2.OC_2H_5)_2Cu_2$, is obtained as an amorphous yellow precipitate on the addition of an ammoniacal solution of cuprous chloride. The ether may be obtained from these derivatives by distilling them with dilute sulphuric acid.

(1591) ETHERS OF THE $(C_nH_{2n-7})_2O$ AND $C_nH_{2n+1}.O.C_nH_{2n-7}$ SERIES.—PHENYLIC ETHER, $(C_6H_5)_2O$.—This ether, which is altogether peculiar in its properties, is obtained on gently warming phenol with diazobenzene sulphate:

$$C_6H_4N_2.H_2SO_4 + C_6H_5.OH = (C_6H_5)_2O + H_2SO_4 + N_2;$$

and is also a product of the destructive distillation of cupric benzoate (Hoffmeister, *Ann. Chem. Pharm.*, clix. 194). It is a colourless crystalline substance, having a pleasant odour resembling that of the geranium, is almost insoluble in water, but easily soluble in alcohol, benzene, or ether; it melts at 28° (82°·4 F.), and boils at 246° (474°·8 F.) It is a body of remarkable stability, for it is not affected by heating with a concentrated solution of hydriodic acid to 250° (482° F.), or by long-continued boiling with a solution of chromic anhydride in glacial acetic acid, or when passed over heated zinc dust; it may be distilled with phosphoric pentachloride without undergoing change, and when heated with it in sealed tubes at 220° (428° F.) is merely chlorinated. It dissolves in concentrated sulphuric acid, forming the disulpho-acid $(C_6H_4.HSO_3)_2O$; concentrated nitric acid converts it into the corresponding dinitro-derivative, which crystallizes in colourless or slightly yellow needles, melting at 135° (275° F.), and distilling at a high temperature unchanged; whilst by adding bromine to its solution in carbonic bisulphide, a crystalline dibromo-derivative is obtained, which melts at 54° (129°·2 F.), and distils without change above 360° (680° F.).

(1592) METHYL PHENYL ETHER OR ANISOL: $CH_3.O.C_6H_5$.—The simplest method of obtaining this ether is to heat in a flask attached to a reversed condenser a mixture of phenol with the amount of potassic hydrate required to convert it into the potassium derivative, a slight excess of methylic iodide, and some methylic alcohol; when the action is complete, the product is separated by the addition of water, and purified by distillation. This method may be employed for the preparation of all the homologous ethers. Methyl phenyl ether may also be obtained by distilling anisic acid with baric hydrate: $C_6H_4(OCH_3).COOH = C_6H_5.OCH_3 + CO_2$, and on this account it is frequently termed anisol.

It is a colourless liquid of pleasant odour, insoluble in water, of the sp. gr. ·991 at 15° (59° F.); it boils at 152° (305°·6 F.). It is a body of very considerable stability, as it resists the action of oxidizing agents, and is not reduced by passing over heated zinc dust—by which treatment phenol is converted into benzene. By heating with a concentrated solution of hydriodic acid at 130° (266° F.), it is resolved into phenol and methylic iodide; hydrobromic and hydrochloric acids decompose it in a similar manner at higher temperatures. When submitted to the action of chlorine or bromine, or of nitric or sulphuric acids, it furnishes substitution derivatives; the haloid phosphorus compounds act in a similar manner (Henry, *Deut. chem. Ges. Ber.*, ii. 710). In all these cases, hydrogen in the C_6 group is alone displaced.

The homologues of methylphenyl ether exhibit very similar properties, but their behaviour on oxidation is different, being similar to that of the hydrocarbons homologous with benzene. Thus, the methyl ethers derived from the three isomeric cresols or methylphenols, $CH_3.C_6H_4.OH$, yield on oxidation the three corresponding methoxybenzoic acids, $C_6H_4(OCH_3).COOH$. This property is of considerable practical value, as it is often possible by first converting the phenols into mixed ethers and oxidizing these latter to ascertain the nature of, and the "position occupied by," the hydrocarbon side chains in the phenols, which cannot be effected by the oxidation of the phenols themselves. For example, by converting phlorol from beech tar creasote (p. 494) into the methyl ether, and oxidizing this latter, Tiemann and Mendelsohn (*Deut. chem. Ges. Ber.*, x. 61) have obtained a methoxyphthalic acid, $C_6H_3(COOH)_2.OCH_3$, thus proving the phenol in question to be a dimethylphenol.

Substitution derivatives of methyl phenyl ether and of the homologous ethers may also be formed from the substitution derivatives of the phenols by the action of the monohaloid derivatives of the paraffins on their metallic derivatives. Thus, by heating the chlorophenols with potassic hydrate and methylic iodide, they are converted into corresponding methyl chlorophenyl ethers, and similarly by the action of methylic or ethylic iodide on the silver derivatives of the nitrophenols, nitrophenyl methyl and ethyl ethers are obtained.

By heating the nitrophenyl ethers with ammonia solution, it is frequently possible to displace the OCH_3 or OC_2H_5 group by the group NH_2, and thus to obtain amido-derivatives corresponding to the phenols from which the ethers were formed; this reaction, which is also of considerable value as a method of ascertaining the constitution of phenol derivatives, apparently only takes place when the OCH_3 group "occupies the para- or ortho-position" relatively to the NO_2 group (comp. p. 333).

(1593) BENZYL ETHERS.—These ethers are obtained by the action of benzylic chloride on the sodium derivatives of the alcohols; for example:

$$C_6H_5.CH_2Cl + C_6H_5.ONa = C_6H_5.O.CH_2.C_6H_5 + NaCl.$$

At present the only interest which attaches to them is on account of their behaviour on chlorination, and with nitric acid, in respect of which they differ somewhat from the ethers of other series. Thus, according to Sintenis (*Ann. Chem. Pharm.*, clxi. 329), when benzyl methyl and ethyl ether are submitted to the action of chlorine either in the cold, or at the boiling temperature, or in presence of iodine, they furnish benzoic aldehyde and a monohaloid paraffin derivative:

$$C_6H_5.CH_2.OC_2H_5 + Cl_2 = C_6H_5.COH + C_2H_5Cl + HCl.$$

They are decomposed in a similar manner by concentrated nitric acid. Benzyl phenyl ether, however, is converted by the action of chlorine or bromine alone, into benzylic chloride or bromide and chlorinated or brominated derivatives of phenol; whilst, if the action take place in presence of mercuric oxide, chlorinated or brominated derivatives of the ether are produced, such as $C_6H_5.CH_2.OC_6H_4Br$, showing that the formation of benzylic chloride, &c., when chlorine alone is employed, is due to the decomposition of the ether by the haloid acid formed in its conversion into haloid substitution derivatives.

(1594) ANETHOL: $C_{10}H_{12}O = CH_3.O.C_6H_4(C_3H_5)$.—This ether is the chief constituent of oil of anise, from which it may be separated by fractional distillation; on cooling the portion collected at about 230°—235° (446°—455° F.), the anethol crystallizes out, and may be purified by crystallization from alcohol. It may be obtained in a similar manner from oil of fennel. Oil of tarragon is said to contain an isomeric substance, and it is also stated that anethol is accompanied by a liquid isomeride in the oils of anise and fennel.

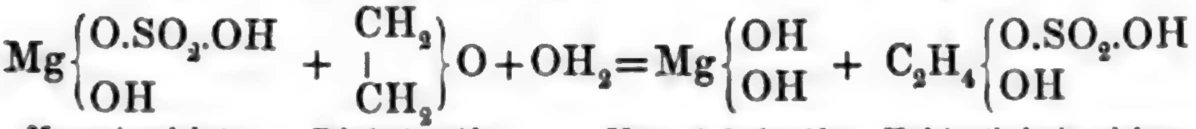
Anethol crystallizes in colourless glistening plates, which melt at 21° (69°·8 F.); it boils at about 232° (449°·6 F.). When boiled with a concentrated solution of hydriodic acid, it furnishes methylic iodide, together with a resinous mass formed from the anol, which is the accessory product of the reaction, and which may be obtained in a pure state by heating anethol to 200°—230° (392°—446° F.) with potassic hydrate (comp. p. 496). It combines with bromine, forming a crystalline dibromide, $CH_3O.C_6H_4.C_3H_5Br_2$; but when submitted to the action of phosphoric pentachloride it furnishes monochloranethol, $C_{10}H_{11}ClO$ (Ladenburg, *Ann. Chem. Pharm. Sup.*, viii. 87). By the action of strong sulphuric acid and of several other reagents, it is converted into what appear to be polymeric substances (Cahours; Kraut and Sehlim, *Jahresb.* 1863, 551; Purenoud, *Ann. Chem. Pharm.*, clxxxvii. 63). On oxidation with nitric or chromic acid, it yields anisic aldehyde, $C_6H_4(OCH_3).COH$, and anisic or paramethoxybenzoic acid, $C_6H_4(OCH_3).COOH$: hence the C_3H_5 and OCH_3 groups in anethol are relatively in the position 1 : 4. The constitution of the C_3H_5 group has not yet been determined (comp. Erlenmeyer, *Deut. chem. Ges. Ber.*, x. 628).

(1595) SIMPLE ETHERS DERIVED FROM POLYHYDRIC ALCOHOLS.—ETHYLENIC OXIDE: C_2H_4O.—This ether, the isomeride of acetic aldehyde, was first described by Wurtz in 1859, who obtained it by the action of potassic hydrate on the chlorhydrin of glycol $CH_2Cl.CH_2.OH$, and very fully investigated its properties. According to Demole (*Ann. Chem. Pharm.*, clxxiii. 125) it is more readily prepared in the following manner:—

A mixture of 1 mol. proportion of *a*-dibromethane (ethylenic bromide), and 2 mol. proportions of *dry* potassic acetate and twice the weight of the latter of 80 per cent. alcohol is heated for 15 hours at 80°—100° (95°—212° F.) in a flask attached to a reversed condenser. The potassic bromide which separates is then filtered off, and the filtrate distilled, first from the water bath, and afterwards from an oil bath. The portion which passes over between 170° and 185° (338°—365° F.), consisting chiefly of the *monacetin* $CH_2(OH).CH_2(C_2H_3O_2)$, is saturated at 100° (212° F.) with hydrochloric acid gas, and the product distilled. The impure *chloracetin*, $CH_2Cl.CH_2(C_2H_3O_2)$, thus obtained is now gradually decomposed with pure potassic hydrate in a capacious flask well cooled externally: the portion boiling at 110°—150° (230°—302° F.) being employed for this purpose; the use of pure alkali is to be recommended, as, if carbonate be present, carbonic anhydride is evolved towards the end of the operation, and occasions the loss of much of the highly volatile ethylenic oxide. When the amount of potassic hydrate added is judged to be sufficient to effect the complete decomposition of the chloracetin, the flask is attached to a reversed condenser which is in connexion with a receiver cooled with a mixture of ice and salt; the flask is then slightly heated so as to cause a regular evolution of gas. This operation requires considerable care, as the disengagement of gas may become so rapid as almost to cause an explosion; but this difficulty may perhaps be obviated by the introduction of sand or pieces of platinum into the flask. According to Demole, it is not advisable to dry the escaping vapours by passing them over potassic hydrate; the dehydration may be readily effected, however, by distilling the product. In this manner from 6–8 grams of the ether may be obtained from 100 grams of bromide.

Ethylenic oxide is a colourless mobile liquid of pleasant odour, miscible in all proportions with water and alcohol; it boils at 13°·5 (56°·3 F.), and at 0° (32° F.) has the sp. gr. ·898. When kept, it sometimes passes spontaneously into a white crystalline polymeride, which is easily soluble in water and alcohol, and melts at 56° (132°·8 F.) (Wurtz, *Compt. Rend.*, lxxxiii. 1141). Ethylenic oxide has marked basic properties, exhibiting in many of its reactions the closest resemblance to the metallic oxides, such as calcic oxide. Thus, it combines slowly with water at ordinary atmospheric temperatures to form the alcohol $CH_2(OH).CH_2(OH)$, and it unites directly with acids, forming with hydrochloric acid, for example, the chlorhydrin $CH_2Cl.CH_2(OH)$, the combination taking place as readily as that of ammonia and hydrochloric acid, and with the oxacids, it yields acid ethereal salts, such as the sulphate, $CH_2(OH).CH_2(O.SO_3H)$, and acetate, $CH_2(OH).CH_2(O.C_2H_3O)$; moreover, it enters into double decomposition with the salts of magnesium, aluminium, iron, copper, and other less positive metals, precipitating the corresponding hydroxides, thus:

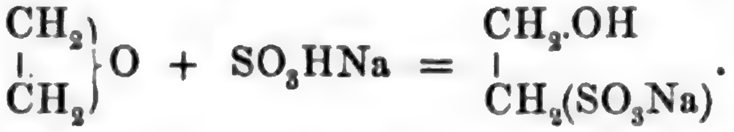
$$MgCl_2 + C_2H_4O + OH_2 = Mg(OH)_2 + C_2H_4Cl.OH.$$



$$Mg\left\{\begin{matrix}O.SO_2.OH\\ OH\end{matrix}\right. + \left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right\}O + OH_2 = Mg\left\{\begin{matrix}OH\\ OH\end{matrix}\right. + C_2H_4\left\{\begin{matrix}O.SO_2.OH\\ OH\end{matrix}\right.$$

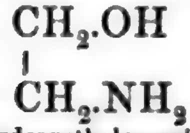
Magnesic sulphate. Ethylenic oxide. Magnesic hydroxide. Hydric ethylenic sulphate.

With acetic anhydride it forms the diacetate (glycol diacetin) $C_2H_4(O.C_2H_3O)_2$, and various acetates of the polyethylenic alcohols, according to the proportions in which it is employed and the temperature to which the mixture is heated; and by heating it to 100° (212°) with hydric sodic sulphite, sodic oxethylsulphonate (isethionate) is produced (Erlenmeyer, *Zeits. Chem.* [2], iv. 342):



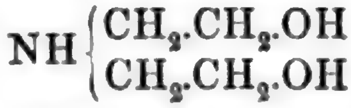
$$\left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right\}O + SO_3HNa = \begin{matrix}CH_2.OH\\ |\\ CH_2(SO_3Na)\end{matrix}.$$

When submitted to the action of nascent hydrogen, it furnishes ethylic alcohol: $C_2H_4O + 2H = C_2H_5.OH$. It combines with sulphuretted hydrogen at 100° (212° F.), forming the thioalcohol $HO.C_2H_4.SH$. It also readily enters into reaction with ammonia and primary amines: thus, when it is mixed with a concentrated aqueous solution of ammonia, a powerful action takes place in a few minutes, and on evaporating the product over the water bath, and saturating the residue with hydrochloric acid, a mixture of the hydrochlorides of mono-, di-, and tri-hydroxethylenamine is obtained (Wurtz). The relation of these compounds to ethylenic oxide will be evident on inspection of the following formulæ:



$$\begin{matrix}CH_2.OH\\ |\\ CH_2.NH_2\end{matrix}$$

Hydroxethylenamine.



$$NH\left\{\begin{matrix}CH_2.CH_2.OH\\ CH_2.CH_2.OH\end{matrix}\right.$$

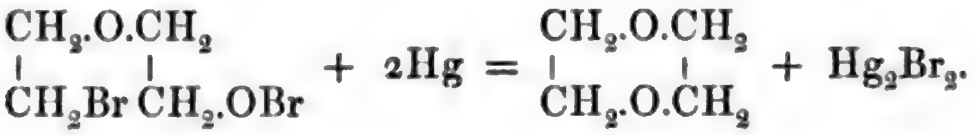
Dihydroxethylenamine.

$$N(CH_2.CH_2.OH)_3.$$

Trihydroxethylenamine.

In a similar manner, when a mixture of ethylenic oxide and aniline or paratoluidine is allowed to stand for some days at the ordinary temperature, the phenyl and tolyl derivatives corresponding to hydroxethylenamine, $C_2H_4(OH).NH.C_6H_5$ and $C_2H_4(OH).NH.C_6H_4.CH_3$, are gradually formed (Demole, *loc. cit.*).

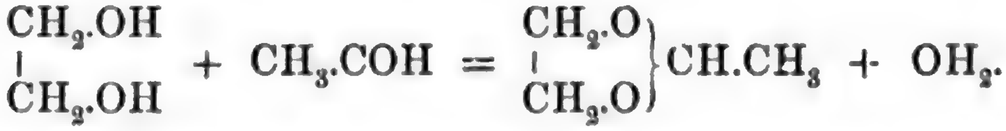
Ethylenic oxide unites with bromine, forming a yellowish-red crystalline compound of the formula $C_4H_8O_2Br_2$, which melts at 65° (149° F.), and boils at 95° (203° F.), yielding an orange-coloured vapour, which condenses to crystals on cooling. By the action of metallic mercury, or of sulphuretted hydrogen, the bromine is readily withdrawn from this compound, and it is converted into *diethylenic dioxide*, the formation of which may be represented by the equation:



$$\begin{array}{ll} CH_2.O.CH_2 & \\ | \quad\quad\;\; | & \\ CH_2Br\,CH_2.OBr & \end{array} + 2Hg = \begin{array}{l} CH_2.O.CH_2 \\ | \quad\quad\;\; | \\ CH_2.O.CH_2 \end{array} + Hg_2Br_2.$$

Below 9° (48°·2 F.) it is a colourless crystalline substance, soluble in water, alcohol, and ether; it boils at 102° (215°·6 F.), and at 0° (32° F.) has the sp. gr. 1·048; it is not altered when heated with ammonia, and acetic anhydride has but little action upon it even at 120° (248° F.). (Wurtz, *Ann. Chem. Pharm.*, cxxii. 354.)

An isomeric compound, *ethylenic ethylidenic dioxide*, is formed on heating a mixture of ethylenic alcohol and aldehyde for some days at 100° (212° F.):

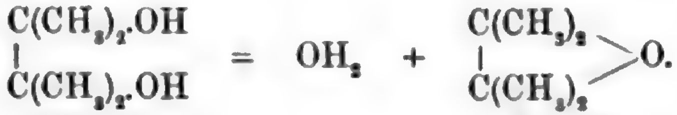


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array} + CH_3.COH = \left.\begin{array}{l} CH_2.O \\ | \\ CH_2.O \end{array}\right\} CH.CH_3 + OH_2.$$

Although formed of the elements of a molecule of ethylenic oxide and of a molecule of aldehyde, this compound apparently cannot be directly obtained by heating these two substances together to 100° (212° F.), the aldehyde being resinified while the ethylenic oxide remains entirely unchanged. It is a colourless liquid, having an agreeable but rather pungent odour, somewhat resembling that of aldehyde, easily soluble in water; it boils at 82°·5 (180°·5 F.), and at 0° (32° F.) has the sp. gr. 1·002. When heated to 140° (284° F.) with acetic acid, it yields glycol diacetin, $C_2H_4(C_2H_3O_2)_2$, together with a much more volatile product having a pungent odour (? crotonic aldehyde). (Wurtz, *ibid.*, cxx. 328.)

(1596) **Homologues of Ethylenic Oxide.**—Very little is known of these compounds. *Propylenic oxide*, C_3H_6O, prepared by the action of potassic hydrate on the chlorhydrin of propylenic glycol, $CH_3.CHCl.CH_2(OH)$, boils at

35° (93° F.), and at 0° (32° F.) has the sp. gr. ·859 (Oser, *ibid.*, *sup.* i. 255); it is converted into isopropylic alcohol by the action of nascent hydrogen (Linnemann). According to Bauer (*ibid.*, cxv. 89), the *amylenic oxide*, $C_5H_{10}O$, prepared from amylenic glycol (from ordinary amylene), boils at about 95° (203° F.); it is insoluble in water, and, when heated with it, is not converted into the glycol; it also does not readily enter into reaction with acetic acid. By the action of argentic oxide on the diiodhexane formed by combining diallyl with hydriodic acid, a *hexylenic oxide*, $C_6H_{12}O$, has been obtained which appears to be identical with that produced by treating diallyl with dilute sulphuric acid (p. 220); it boils at 93°—95° (199°·4—203° F.). A number of homologues of ethylenic oxide which are probably all of similar constitution may be obtained by heating the pinacones or dihydric alcohols of the composition $[C(C_nH_{2n+1})_2.OH]_2$ with dilute sulphuric acid; thus:



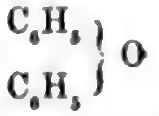
$$\begin{matrix} C(CH_3)_2.OH \\ | \\ C(CH_3)_2.OH \end{matrix} = OH_2 + \begin{matrix} C(CH_3)_2 \\ | \\ C(CH_3)_2 \end{matrix} \!>\! O.$$

Pinacone. Pinacolin.

These pinacolins are chiefly of interest on account of their behaviour with nascent hydrogen, and will be again referred to when the ketones are described.

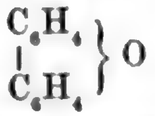
(1597) GLYCERIC ETHER OR ALLYLIC TRIOXIDE: $(C_3H_5)_2O_3$.—This compound, which may be regarded as the analogue of bismuthic trioxide, appears to be formed on distilling glycerol with calcic chloride, and as a by product in the preparation of allylic alcohol from glycerol and oxalic acid. It is a colourless, slightly viscid liquid, having a mint-like odour, soluble in about twenty parts of water; it boils at 169°—173° (336°·2—343°·4 F.). By heating with water to 140° (284° F.), it is reconverted into glycerol (Linnemann and Zotta, *ibid.*, *sup.* viii. 257; Tollens, *Deut. chem. Ges. Ber.*, v. 68).

No simple ethers derived from the orcinols in the same manner that ethylenic oxide is derived from glycol have been prepared; such compounds, in fact, are generally supposed to be incapable of existing, as all attempts to obtain bodies formed by the displacement of more than one hydrogen atom in benzene and analogous hydrocarbons by the same radicle have been unsuccessful. The only ether which remains to be mentioned is *diphenylenic oxide*, $C_{12}H_8O$, which is obtained by distilling phenylic phosphate with a large excess of lime (Hoffmeister, *ibid.*, clix. 211). It crystallizes from alcohol in small colourless plates having a pleasant odour, which melt at about 80° (176° F.); it boils at about 273° (523°·4 F.). It is a body of remarkable stability, closely resembling phenyl ether, from which it may be regarded as derived by the withdrawal of two atoms of hydrogen; thus:



$$\left.\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\right\} O$$

Diphenyl oxide.



$$\left.\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\right\} O$$

Diphenylene oxide.

(1598) MIXED ETHERS DERIVED FROM POLYHYDRIC AND MONOHYDRIC ALCOHOLS.—These compounds, of which but few are known, are the analogues of the mixed oxides, such as sodic zincic oxide (sodic zincate), $Zn(ONa)_2$, formed by the action upon each other of the oxides or hydroxides of a more and of a less positive metal. Those derived in this manner from the glycols and the alcohols of the ethylic series are prepared by the action of the monohaloid derivatives of the paraffins on the disodium derivatives of the glycols, or on the monosodium derivatives of the ether-alcohols, $C_nH_{2n}(OH).C_nH_{2n}(OC_nH_{2n+1})$, derived from the glycols, the latter being a method which may be employed for the preparation of ethers containing three dissimilar radicles; for example:

$$\underset{\text{Disodic ethylenate.}}{C_2H_4(ONa)_2} + 2C_2H_5I = \underset{\text{Ethylene diethyl ether.}}{C_2H_4(OC_2H_5)_2} + 2NaI.$$

$$\underset{\text{Sodic ethylic ethylenate.}}{CH_2(ONa).CH_2(OC_2H_5)} + CH_3I = \underset{\text{Ethylene methyl ethyl ether.}}{CH_2(OC_2H_5).CH_2(OCH_3)} + NaI.$$

A number of mixed ethers derived in a similar manner from the aldehydrols isomeric with the glycols are obtained by the direct action of the aldehydes of the acetic series on the alcohols of the ethylic series; these ethers are frequently termed acetals:

$$\underset{\text{Aldehyde.}}{CH_3.COH} + 2C_2H_5.OH = OH_2 + \underset{\text{Ethylidene diethyl ether.}}{CH_3.CH(OC_2H_5)_2}.$$

The ethers thus formed from the dihydric alcohols of the $C_nH_{2n}(OH)_2$ series are colourless liquids of agreeable odour, and exhibit the closest resemblance in properties to the mixed ethers derived from monohydric alcohols of the $C_nH_{2n+1}.OH$ series.

On the other hand, those derived from the glycols and phenols, of which ethylenediphenyl ether formed by the action of α-dibromethane on sodium phenol: $C_2H_4Br_2 + 2C_6H_5.ONa = C_2H_4(OC_6H_5)_2 + 2NaBr$, is an example, manifest properties similar to those of anisol or methyl phenyl ether.

Ethylene diethyl ether, $CH_2(OC_2H_5).CH_2(OC_2H_5)$, is a mobile, colourless liquid, having a fragrant ethereal odour; it boils at 123°·5 (253°·4 F.). The isomeric *ethylidene diethyl ether* or *acetal*, $CH_3.CH(OC_2H_5)_2$, which is one of the products of the incomplete oxidation of alcohol, but is more readily prepared by heating a mixture of aldehyde and anhydrous alcohol at 100° (212° F.), boils at about 105° (221° F.).

These two ethers cannot be advantageously prepared from sodic ethylate and the corresponding dibromethanes, as these latter are chiefly converted into bromethylene when thus treated; and whereas a certain amount of acetal is formed from β-dibromethane (ethylidene bromide), the corresponding β-dichlorethane furnishes only monochlorethylene when submitted to the action of sodic ethylate.

The only homologues of acetal at present known are *methylene dimethyl ether* or *methylal* (*formal*), $CH_2(OCH_3)_2$, which is obtained in small quantity by distilling methylic alcohol with sulphuric acid and manganic peroxide; *ethylidene dimethyl ether*, $CH_3.CH(OC_2H_3)_2$, prepared in a similar manner from a mixture of methylic and ethylic alcohol, but more readily obtained by heating aldehyde with anhydrous methylic alcohol; and *ethylidene methyl ethyl ether*, $CH_3.CH\left\{\begin{matrix}OCH_3\\OC_2H_5\end{matrix}\right.$, which is formed together with the last-mentioned ether on oxidizing a mixture of methylic and ethylic alcohols. They are colourless liquids like acetal, the first of which boils at 42° (107°·6 F.), the second at about 64° (147°·2 F.), and the third at about 85° (185° F.); methylal dissolves in thrice its volume of water, but may be separated from the solution by the addition of caustic alkali; the homologous ethers diminish in solubility as their molecular weight increases.

The ethers derived from the glycols are much more stable compounds than the isomeric ethers derived from the aldehydrols. Like most ethers, both of them resist the action of alkalies, but are without difficulty decomposed by acids; thus, on heating acetal with glacial acetic acid, it yields ethylic acetate and aldehyde. By carefully mixing the acetals with concentrated sulphuric acid, solutions are obtained which appear to contain the corresponding aldehydrols—or acid sulphates formed from them—which may often be employed in effecting reactions which cannot be realized by directly employing the aldehydes; but the aldehydes cannot as a rule be separated from these solutions since they rapidly undergo change under the influence of the acid:

$$\underset{\text{Acetal.}}{CH_3.CH(OC_2H_5)_2} + 2H_2SO_4 = \underset{\text{Aldehydrol.}}{CH_3.CH(OH)_2} + 2C_2H_5.HSO_4.$$

When exposed to moist air in contact with platinum black, the acetals readily absorb oxygen, and are converted first into the corresponding aldehydes, and then into acids of the acetic series.

It has already been pointed out (p. 429) that when chlorine is passed into aqueous alcohol, acetal is produced; Lieben and Paterno have shown that if the action of chlorine be continued, mono-, di- and tri-chloracetal are formed. If pure acetal be submitted to the action of chlorine, much heat is developed, the chlorine being absorbed with avidity; if the acetal be carefully cooled, the whole of the hydrochloric acid remains in solution, but on distilling the product when the amount of chlorine absorbed corresponds to that required for the formation of monochloracetal, it is found that one half the acetal is unaffected, and that the product consists almost entirely of the dichlorinated derivative (Pinner, *Deut. chem. Ges. Ber.*, v. 147). *Monobromacetal*, however, is readily produced on mixing bromine with well cooled acetal in the required proportions; and monochloracetal may be prepared by heating dichlorether (p. 672) with sodic ethylate.

Monochloracetal: $CH_2Cl.CH(OC_2H_5)$, boils at 157° (314°·6 F.). *Monobromacetal:* $CH_2Br.CH(OC_2H_5)_2$, is a colourless liquid insoluble in water, boiling with partial decomposition at 170° (338° F.); by heating it for twelve hours at 160°—180° (320°—356° F.) with an alcoholic solution of potassic hydrate, it is converted into the ether-alcohol $CH_2(OH).CH(OC_2H_5)_2$, the ethylic derivative of which is produced on heating bromacetal to 160° (320° F.) with a concentrated solution of sodic ethylate. Both are colourless liquids of agreeable odour, boiling at 167° (332°·6 F.) and 164° (327°·2 F.) respectively; they are completely decomposed by strong acids, without, however, furnishing well characterized products.

Dichloracetal: $CHCl_2.CH(OC_2H_5)_2$, is a colourless liquid which boils at 180° (356° F.); on distillation with sulphuric acid, it furnishes dichloraldehyde, $CHCl_2.COH$; and by the action of sodic ethylate at 160° (320° F.), it is converted into the ether $CH(OC_2H_5)_2.CH(OC_2H_5)_2$ derived from ethylic alcohol and the tetrahydric alcohol (dialdehydrol) $CH(OH)_2.CH(OH)_2$; this ether is a colourless fragrant liquid, insoluble in, and lighter than, water, and boils at about 180° (356° F.) without undergoing decomposition (Pinner, *loc. cit.*).

Trichloracetal is formed, although in small quantity, together with dichloracetal, by the action of chlorine on common alcohol at 80° (176° F.), and may be separated by fractional distillation; it crystallizes in needles, which melt at 72° (161°·6 F.), and boils with slight decomposition at 230° (446° F.). This compound is perhaps represented by the formula $CHCl_2.CCl(OC_2H_5)_2$, as it is isomeric with the trichloracetal produced on heating tetrachlorether (p. 672), $CCl_3.CHCl(OC_2H_5)$, with alcohol in sealed tubes at 100° (212° F.) and which therefore has the formula $CCl_3.CH_2 (OC_2H_5)_2$; this latter is a colourless liquid, which boils at 205° (401° F.); when decomposed with water or sulphuric acid it furnishes trichloraldehyde (Paterno and Pisati, *Gaz. chim. ital.*, ii. 333; Wurtz and Vogt, *Compt. Rend.*, lxxiv. 277).

(1599) ETHERS DERIVED FROM THE ORCINOLS AND ALCOHOLS OF THE ETHYLIC SERIES.—These ethers are prepared, either by heating an intimate mixture of an orcinol with potassic hydrate and methylic potassic sulphate or one of its homologues in sealed tubes to about 160° (320° F.); or by heating the orcinols with potassic hydrate and an iodoparaffin at 100°—120° (212°—248° F.);

or by digesting the sodium or potassium derivatives of the ether alcohols, such as methylcatechol (guaiacol), $C_6H_4(OH).OCH_3$, with an iodoparaffin and the corresponding alcohol—this last being used merely as a solvent. By the first mentioned method, Hlasiwetz and Habermann (*Ann. Chem. Pharm.*, clxxvii. 340) and Habermann (*Deut. chem. Ges. Ber.*, x. 867) respectively have prepared the dimethyl-derivatives of quinol (hydroquinone) and resorcinol; the second has been employed by de Luynes and Lionet (*Compt. Rend.*, lxv. 213) in preparing the derivatives of orcinol; and dimethylcatechol (dimethylpyrocatechin) and dimethylhomocatechol have been prepared by the last mentioned method, the former having also been obtained by distilling the modification of dimethoxybenzoic acid derived from protocatechuic acid with lime. With the exception of the quinol derivative, which is a crystalline solid, melting at 55°—56° (131°—132°·8 F.), they are said to be colourless, highly refractive liquids of not unpleasant odour, insoluble in water; their boiling points are as follows:

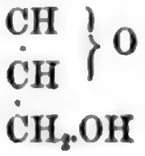
		B. P. °C.
Orthodimethoxybenzene, or catechol dimethylin .	$C_6H_4(OCH_3)_2$	205°—206°
Metadimethoxybenzene, or resorcinol dimethylin .		214°—215°
Paradimethoxybenzene, or quinol dimethylin . .		204°—205°
Orcinol dimethylin	$CH_3.C_6H_3(OCH_3)_2$	240°—250°
Homocatechol dimethylin		214°—218°

According to Koerner, the so-called *Veratrol*, $C_8H_{10}O_2$, which is obtained on submitting a mixture of veratric acid, $C_9H_{10}O_4$, and baryta to dry distillation, is catechol dimethylin, veratric acid being identical with dimethyl-protocatechuic acid. It is a crystalline substance, of pleasant aromatic odour, which melts at 15° (59° F.), and boils at about 205° (401° F.). It furnishes crystalline nitro- and bromo-derivatives (Merck, *Ann. Chem. Pharm.*, cviii. 58; Koerner, *Gaz. chim. ital.*, vi. 142).

According to de Luynes and Lionet, it is possible to displace *three* atoms of hydrogen in orcinol by methyl or ethyl by heating it with a large excess of potassic hydrate and of methylic or ethylic iodide; the trimethyl derivative is said to boil at about 250° (482° F.), and the triethyl derivative at about 265° (509° F.). The formation of ethers derived from homologues of orcinol in this manner appears highly remarkable, and, as the reaction is without precedent, it is especially deserving of further investigation.

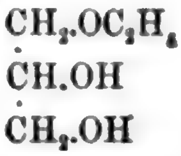
§ II. Ether-Alcohols.

The ether-alcohols are compounds formed from polyhydric alcohols either by the abstraction of the elements of one or more molecules of water, in such proportions, however, that one or more of the hydroxyl groups remain unaffected, or by the displacement of one or more, but not all, of the hydrogen atoms in the OH groups by the so-called alcohol radicles. They therefore still exhibit the characteristic properties of alcohols, although necessarily of alcohols of lower hydricity than the polyhydric alcohols from which they are derived. The so-called glycide, and the mon- and di-ethylins of glycerol (glycerin) are examples of the two classes of ether-alcohols:



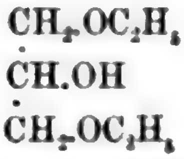
$$\left.\begin{matrix}CH\\ \dot{C}H\end{matrix}\right\}O \\ \dot{C}H_2.OH$$

Glycide.



$$\begin{matrix}CH_2.OC_2H_5\\ \dot{C}H.OH\\ \dot{C}H_2.OH\end{matrix}$$

Glycerol-monethylin.



$$\begin{matrix}CH_2.OC_2H_5\\ \dot{C}H.OH\\ \dot{C}H_2.OC_2H_5\end{matrix}$$

Glycerol-diethylin.

(1600) Glycide: $C_3H_6O_2$.—To prepare this compound, epichlorhydrin (p. 542) is heated with potassic acetate, and the product submitted to fractional distillation; the portion which boils at about 168° (334°·4 F.), consisting of the acetate $C_3H_5O(C_2H_3O_2)$, is dissolved in ether, decomposed by pulverized sodic hydrate, and the glycide separated by distillation. It is a mobile liquid, boiling at about 162° (323°·6 F.), soluble in all proportions in water, alcohol, and ether; it is converted into glycerol by the action of water at 100° (212° F.), and readily combines with hydrochloric acid (Gegerfelt, *Bull. Soc. Chim.* [2], xxiii. 160).

The so-called mannitane and dulcitane produced by heating mannitol and dulcitol, and by the action of alkalies on the chlor- and brom-hydrins of these alcohols belong to the class of ether-alcohols; but little is known of their properties, however, and it is even doubtful whether they have been prepared in a pure state, as they are all amorphous substances (comp. Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 146).

(1601) Ether-alcohols derived from Dihydric Alcohols of the $C_nH_{2n}(OH)_2$ Series.—*Glycol Monethylin*: $CH_2(OH).CH_2(OC_2H_5)$.—This compound is prepared by dissolving sodium in glycol, and heating the resulting monosodium glycol with ethylic iodide. The homologous compounds could doubtless be obtained in a similar manner. It is also formed by the direct combination of ethylenic oxide with ethylic alcohol. It is a colourless liquid of pleasant ethereal odour, and boils at 127° (260°·6 F.).

Corresponding compounds derived from the aldehydrols do not appear to be capable of existing, but their chlorinated derivatives may readily be obtained by combining chlorinated aldehydes of the $C_nH_{2n+1}.COH$ series with the alcohols of the ethylic series. Thus on mixing trichloraldehyde or chloral, $CCl_3.COH$, with absolute alcohol, a considerable amount of heat is developed, and after a time the mixture solidifies to a mass of crystals of the monethylin of trichloraldehydrol (so-called *chloral-alcoholate*), $CCl_3.CH(OH).OC_2H_5$. This compound melts at 56° (132°·8 F.), and boils at about 115° (239° F.), but the vapour appears to consist of a mixture of chloral and alcohol; on treatment with acetic chloride it is converted into the acetate $CCl_3.CH(OC_2H_5).C_2H_3O_2$, and when distilled with phosphoric pentachloride it furnishes tetrachlorether (p. 672).

The homologous compounds may be obtained by employing the homologues of ethylic alcohol. According to Henry (*Deut. chem. Ges. Ber.*, vii. 763), the more positive the alcohol radicle, the greater the heat developed in their formation, more heat, for example, being developed by the union of chloral with methylic than with ethylic alcohol. Like the ethylin, these compounds all undergo dissociation when converted into vapour; they are readily decomposed by sulphuric acid, yielding chloral and an acid ethereal sulphate; and they are also readily decomposed by caustic alkalies: they are, in fact, far less stable bodies than the ether-alcohols derived from the glycols, which may be volatilized unchanged. Chloral also forms a crystalline ether-alcohol with mercaptan, the composition of which is either $CCl_3.CH(SH).OC_2H_5$ or $CCl_3.CH(OH).SC_2H_5$ (Martius and Mendelssohn-Bartholdy, *ibid.*, iii. 443).

(1602) Ether-alcohols derived from the Dihydric Alcohols of the $C_nH_{2n-8}(OH)_2$ Series.—A number of ether-alcohols derived from the orcinols and alcohols of the ethylic series have been prepared by heating the orcinols with potassic hydrate and methylic potassic sulphate or the moniodoparaffins. The monomethylins of catechol and homocatechol are the principal constituents of wood tar creasote, and are known respectively as guaiacol and creosol.

Guaiacol or Catechol Monomethylin: $C_6H_4(OH).OCH_3$ ($OH : OCH_3 = 1:2$), is the chief constituent of the portion of creasote which boils at about 200° (392° F.); it may be artificially prepared by heating a mixture of the theoretical proportions of catechol (pyrocatechin), potassic hydrate, and potassic methylic sulphate, in sealed tubes, at 170°—180° (338°—356° F.) (Gorup-Besanez, *Ann. Chem. Pharm.*, cxlvii. 247). Guaiacol is a colourless liquid, having a peculiar pleasant aromatic odour, and burning taste; it boils at about 199° (390°·2 F.). It is almost insoluble in water, but dissolves readily in alcohol and ether. When mixed with an alcoholic solution of ferric chloride it produces an emerald-green colour. Potassium and sodium dissolve in it, forming corresponding metallic derivatives; when mixed with ammonia, it solidifies to a crystalline mass; whilst with ether and a concentrated alcoholic solution of potassic hydrate, a crystalline potassium derivative of the composition $C_7H_7KO_2,C_7H_8O_2 + OH_2$ is obtained. It also yields crystalline metallic derivatives containing metals of the alkaline earths. These metallic derivatives are all very soluble in water, and also dissolve in alcohol and ether, but their solutions are extremely unstable, and readily decompose on exposure to the air. Guaiacol reduces gold and silver salts to the metallic state. When heated with hydriodic acid, it yields catechol and methylic iodide; and by distilling it over heated zinc dust, methyl phenyl ether, or anisol, $C_6H_5.OCH_3$, is produced.

Creosol or Homocatechol Monomethylin: $CH_3.C_6H_3(OH).OCH_3$, which is chiefly contained in the portion of creosote boiling at about 220° (428° F.), manifests the closest resemblance in its properties to catechol. By converting it into the dimethyl ether, $CH_3.C_6H_3(OCH_3)_2$, by digesting its potassium derivative with methylic iodide, oxidizing this ether with potassic permanganate, and fusing the resulting dimethoxybenzoic acid with potassic hydrate, &c., the modification of dioxybenzoic acid known as protocatechuic acid is obtained, thus proving that the methyl and OH groups in homocatechol occupy the relative positions $CH_3 : OH : OH = 1 : 3 : 4$ (Tiemann and Mendelsohn, *Deut. chem. Ges. Ber.*, viii. 1136); and by oxidizing acetocreosol, $CH_3.C_6H_3(OCH_3).C_2H_3O_2$, with potassic permanganate, and subsequently displacing the acetyl group in the resulting acid by hydrogen by heating it carefully with sodic hydrate, *vanillic acid*, $C_6H_3(OH)(OCH_3).COOH$, is obtained, in which (q.v.) the OCH_3 group has been shown to occupy the meta position relatively to the COOH group: hence the constitution of creosol is represented in the formula $CH_3 : OCH_3 : OH = 1 : 3 : 4$ (*ibid.*, x. 58).

The *monomethylin* of *resorcinol* is a liquid which may be cooled to − 17°·5 (·5° F.) without solidifying; it boils at about 244° (471°·2 F.), and unlike guaiacol does not volatilize in a current of steam. Its aqueous solution is coloured violet by ferric chloride (Habermann, *ibid.*, x. 868).

Quinol (hydroquinone) *monomethylin* forms prismatic crystals, which melt at 53° (127°·4 F.); it boils at about 243° (469°·4 F.), and is but slightly volatile in a current of steam. It is obtained, together with quinol and a glucose, on heating arbutin with dilute sulphuric acid, and may be prepared artificially by heating quinol with potassic hydrate and potassic methylic sulphate (Hlasiwetz and Habermann, *Ann. Chem. Pharm.*, clxxvii. 334).

The monomethylin and monethylin of orcinol are said to be liquid substances (de Luynes and Lionet).

(1603) EUGENOL: $C_3H_5.C_6H_3(OH).OCH_3$.—This compound is the chief constituent of oil of cloves. It is a colourless, highly refractive liquid, of pleasant aromatic odour; it boils at 247°·5 (477°·5 F.), but on distillation is partially converted into a resinous polymeride. It has the sp. gr. 1·0779 at 0° (32° F.), and 1·0630 at 18°·5 (65°·3 F.). It dissolves in alcohol, ether, and acetic acid, but is almost insoluble in water; the alcoholic solution is coloured blue by ferric chloride. Although without action on vegetable colours, it dissolves in alkalies, and furnishes a number of crystalline metallic derivatives corresponding in composition to the potassium derivative $C_3H_5.C_6H_3(OK).OCH_3$. When it is heated with hydriodic acid, methylic iodide is produced. On digestion with potassic hydrate and ethylic bromide it is converted into the ether $C_3H_5.C_6H_3(OC_2H_5).OCH_3$; this boils at 254° (489°·2 F.), but is partially converted into a crystalline polymeride, melting at 125° (257° F.). When oxidized with chromic acid mixture, it is converted into the acid $C_6H_3(OCH_3)(OC_2H_5).COOH$, which yields protocatechuic acid, $C_6H_3(OH)_2.COOH$, on digestion with hydriodic acid solution at 120°—130° (248°—266° F.) (Erlenmeyer and Wassermann, *Ann. Chem. Pharm.* clxxix. 366). By digesting eugenol with acetic anhydride, acetoeugenol, $C_3H_5.C_6H_3(OCH_3)C_2H_3O_2$, is produced, which on oxidation with potassic permanganate yields a mixture of the acetyl derivatives of *vanillin*, $C_6H_3(OH)(OCH_3)COH$, *vanillic acid*, $C_6H_3(OH)(OCH_3).COOH$, and of the homologous acid *a-homovanillic acid*, $C_6H_3(OH)(OCH_3).CH_2.COOH$ (Tiemann and Nagai, *Deut. chem. Ges. Ber.*, ix. 52, 418; x. 201). The formation of protocatechuic acid and of vanillin (q.v.) from eugenol is a proof that the side chains are relatively in the position $C_3H_5 : OCH_3 : OH = 1 : 3 : 4$, whilst the formation of a-homovanillic acid renders it not improbable that the C_3H_5 group has the constitution $CH_2.CH{=}CH_2$.

(1604) ETHER-ALCOHOLS DERIVED FROM GLYCEROL.—These compounds are formed by the action of the sodium derivatives of alcohols of the ethylic and other series on the chlorhydrins of glycerol (glycerin), but, as yet, very few have been prepared. Thus by the action of sodic ethylate on the monochlorhydrin, the *monethylin* $C_3H_5(OH)_2.OC_2H_5$ is produced, and the dichlorhydrin may be converted into the *diethylin* $C_3H_5(OH)(OC_2H_5)_2$ in a similar manner; both are liquid substances, and boil respectively at about 230° (446° F.) and 191° (375°·8 F.). By dissolving sodium in the latter, and then submitting the product to the action of ethylic iodide, the *triethylin* $C_3H_5(OC_2H_5)_3$ is produced, which boils at about 185° (365° F.). The first of these compounds is soluble in water, the second is but slightly soluble, and the third insoluble. Glycerol triethylin and the homologous compounds may also be obtained by heating acrylic aldehyde with the alcohols of the ethylic series (Ahlsberg, *Jahresb.*, 1864, 494).

By the withdrawal of the elements of a molecule of water from glycerol monethylin and its homologues, a series of ethers derived from glycid may be obtained: $C_3H_5(OH)_2.OC_2H_5 - OH_2 = C_3H_5O.OC_2H_5$.

These ethers are prepared by the action of potassic or sodic hydrate on the chlorinated compounds formed from the monethylin, &c., by displacing one of the two OH groups by chlorine; these latter bodies being obtained either by the action of hydrochloric acid on the monethylin or one of its homologues, or by heating a mixture of epichlorhydrin and an alcohol of the ethylic series, or by combining the ether of the $C_3H_5.OC_nH_{2n+1}$ series with hypochlorous acid.

Ethyl glycidic ether, $C_3H_5O.OC_2H_5$, is a colourless liquid of pleasant ethereal odour, and pungent taste, boiling at about 128° (262°·4 F.). The glycidic ethers combine with the haloid acids, even at ordinary temperatures, and at more elevated temperatures with water and the oxacids in precisely the same manner as bodies like glycid and epichlorhydrin (Reboul, *Ann. Chem. Pharm.*, sup. i. 218; Henry, *Deut. chem. Ges. Ber.*, v. 449).

The crude allylic alcohol obtained by distilling a mixture of glycerol and oxalic acid contains a substance of high boiling point, which is apparently the *monallylin* of glycerol, $C_3H_5(OH)_2.OC_3H_5$; it is a viscid liquid, soluble in water, but separable from the solution by the addition of potassic carbonate. On distillation it boils at 225°—240° (437°—464° F.), but is partially decomposed with formation of allylic alcohol. It combines with bromine (Tollens, *Deut. chem. Ges. Ber.*, v. 68).

(1605) ETHER-ALCOHOLS DERIVED FROM PYROGALLOL.—By heating a mixture of pyrogallol, potassic hydrate, potassic ethylic sulphate and absolute alcohol in closed vessels at 100° (212° F.). Benedikt (*ibid.*, ix. 125) has obtained a mixture of the mon- and di-ethylin. *Pyrogallol monethylin*, $C_6H_3(OH)_2.OC_2H_5$, crystallizes from water, in which it is difficultly soluble, in fine needles which melt at 95° (203° F.). *Pyrogallol diethylin*, $C_6H_3(OH)(OC_2H_5)_2$, is liquid even at —10° (14° F.); it boils at 262° (503°·6 F.). Both compounds are volatile with the vapour of water. Ethylic iodide is entirely without action on pyrogallol at 120° (248° F.).

At present we are not acquainted with any ether-alcohols derived from tetra-, penta- or hexahydric alcohols.

§ III. The Glucosides.

(1606) This name is applied to a large number of bodies having the one property in common of furnishing a *glucose* and one or more other products when heated with water and an acid, their decomposition in this manner being invariably the consequence of the addition of the elements of water to the compound, which becomes thereby resolved into simpler compounds; thus salicin, when heated with dilute hydrochloric or sulphuric acid, is converted into a dextroglucose and the alcohol saligenol (saligenin):

$$\underset{\text{Salicin.}}{C_{13}H_8O_7} + OH_2 = \underset{\text{Saligenol.}}{C_6H_4(OH).CH_2(OH)} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

This behaviour indicates the close connexion of the glucosides with the ethers and ether-alcohols.

The resolution of many of the glucosides into glucose, &c., may be effected at ordinary temperatures by the aid of certain so-called unorganized ferments acting in presence of water, these ferments being mostly met with in the same plant as the glucosides they are capable of decomposing. The power of these ferments to induce decomposition is usually restricted, however, a given ferment having only the power of influencing the decomposition of a limited number of more or less closely related glucosides.

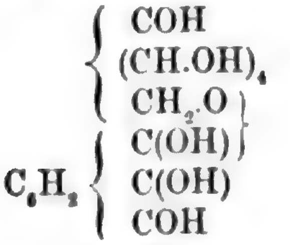
In a few cases, it has been shown that the glucose furnished by certain glucosides is sucrodextrose, but in the majority of cases the glucose produced has not been sufficiently examined to establish its identity, and a more careful study of the glucoses from the various glucosides is much to be desired (comp. p. 582). The accessory product or products furnished by the glucosides are of the most diverse character; in fact, of the large number of compounds included in the group, the majority bear little or no relation to each other in constitution.

The following account refers chiefly to the better known glucosides, which are described in alphabetical order:

Æsculin: $C_{15}H_{16}O_9$.—This glucoside is found in the bark of the horse chestnut, and in other species of *Æsculus* and *Pavia*, where, according to Stokes, it exists associated with another fluorescent compound, *paviin*, which closely resembles æsculin, but is much more soluble in ether. Æsculin may readily be prepared by precipitating a decoction of horse chestnut bark with alum and a slight excess of ammonia, evaporating the clear solution to dryness at 100° (212° F.) and extracting with boiling alcohol. The crystals obtained on concentrating the extract are purified by recrystallization. It crystallizes in colourless needles which have a bitter taste, and melt at about 160° (320° F.). It is almost insoluble in ether, and only slightly soluble in cold water or alcohol; it dissolves more readily in boiling water or alcohol. The solutions exhibit a beautiful sky-blue fluorescence, which is augmented by alkalies, but is destroyed by acids. With plumbic subacetate, it gives a yellow precipitate. By boiling with acetic anhydride it is converted into *hexacetylæsculin*, $C_{15}H_{10}(C_2H_3O)_6O_9$, whilst with aniline it gives *trianilæsculin*, $C_{15}H_{16}O_6(C_6H_5.N)_3$.

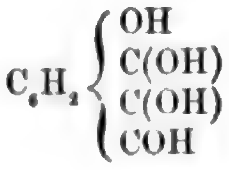
Æsculin, when boiled with dilute sulphuric or hydrochloric acid, or when submitted to the action of emulsin, is decomposed, yielding *æsculetin* and a glucose: $C_{15}H_{16}O_9 + OH_2 = C_9H_6O_4 + C_6H_{12}O_6$. On concentrating the solution and allowing it to cool, the æsculetin is deposited in the crystalline state. When pure, it forms colourless silky needles and plates containing water of crystallization, which they lose at 100° (212° F.). It then melts above 270° (518° F.), and distils without decomposition at a higher temperature. Æsculetin is but very slightly soluble in cold water or alcohol, and almost insoluble in ether. It is readily soluble, however, in dilute alkaline solutions, but is reprecipitated unchanged on the addition of an acid. Plumbic acetate precipitates its solutions of a pale yellow colour. Its aqueous solution is coloured dark green by ferric chloride. By the action of acetic anhydride or chloride, or of anilin, æsculetin is converted into *triacetylæsculetin*, $C_9H_3(C_2H_3O)_3O_4$, or into *trianilæsculetin*, $C_9H_6O(C_6H.N)_3$. When æsculetin is heated with potassic hydrate it yields formic and protocatechuic acids: (?) $C_9H_6O_4 + 2OH_2 + O_2 = C_6H_3(OH)_2.COOH + 2CH_2O_2$.

On boiling æsculetin with hydric sodic sulphite, it is converted into an isomeric body, which combines with the sulphite to form a crystalline compound of the formula $2C_9H_6O_4,HNaSO_3 + OH_2$. On decomposing this with dilute sulphuric acid, &c., the new compound, *paræsculetin*, is liberated. It is extremely soluble in water, from which it may be obtained in indistinct crystals having the formula $2C_9H_6O_4,5OH_2$. Exposed to the action of ammonia, it becomes first red, then violet, and ultimately sky-blue. Rochleder assigns to this blue compound the formula $C_9H_7NO_5$, and from its analogy to orcein, calls it *æsorceïn*. Paræsculetin is not acted on by acetic anhydride, but is more readily converted into the trianilid, $C_9H_6O(C_6H_5.N)_3$ than æsculetin. It is an extremely powerful reducing agent, precipitating cuprous oxide from cupric tartrate solution, even in the cold. Schiff (*Ann. Chem. Pharm.*, clxi. 71) has suggested that the constitution of æsculin, æsculetin, and paræsculetin, may be expressed by the following formulæ:



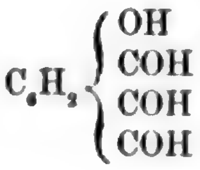
$$\left\{\begin{array}{l} COH \\ (CH.OH)_4 \\ \left.\begin{array}{l} CH_2.O \\ C(OH) \end{array}\right\} \end{array}\right. \qquad C_6H_2\left\{\begin{array}{l} C(OH) \\ C(OH) \\ COH \end{array}\right.$$

Æsculin.



$$C_6H_2\left\{\begin{array}{l} OH \\ C(OH) \\ C(OH) \\ COH \end{array}\right.$$

Æsculetin.



$$C_6H_2\left\{\begin{array}{l} OH \\ COH \\ COH \\ COH \end{array}\right.$$

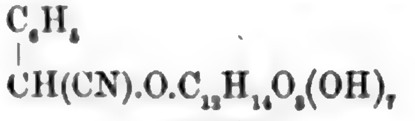
Paræsculetin.

These formulæ, however, are not altogether in accordance with what is known of the bodies in question. Thus Schiff has himself shown that acetic anhydride is without action on paræsculetin, whereas a compound having the above formula should yield a monacetyl derivative. Moreover, the group C.OH is a dyad radicle, and unless it be supposed that the two C.OH groups which, according to Schiff, are to be assumed as present in æsculin and æsculetin, are in combination, these compounds must be regarded as primarily derived from a hydrocarbon C_6H_8, whereas paræsculetin, according to Schiff's formula, would be a benzene derivative; but it is not probable that a benzene derivative would be formed from a derivative of the hydrocarbon C_6H_8 by the action of a powerful reducing agent like hydric sodic sulphite.

According to Rochleder, there are in the seeds of the horse chestnut numerous other substances allied to æsculetin, or which may be obtained from it by the action of various reagents, such as *æscigenin*, *argyræscin*, *æscinic acid*, *aphrodescin*, *æscorcin*, &c. (*Bull. Soc. Chim.* [2], ix. 383).

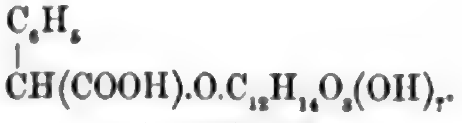
Amygdalin: $C_{20}H_{27}NO_{11}$.—This glucoside is contained in the leaves and other parts of many of the *Amygdalaceæ* and *Pomaceæ* and other plants which furnish hydrocyanic acid on distillation with water, but especially in bitter almonds, from which it may readily be obtained by expressing the oil, extracting the paste with alcohol, decanting from any oil that may be deposited, and then concentrating the extract by distillation to about half its volume. On adding ether to the solution, the amygdalin is precipitated, and may be purified by crystallization from boiling alcohol. It forms pearly scales, which are insoluble in ether, but very soluble in water, crystallizing from the latter in slender prisms containing 3 mols. of water of crystallization; the aqueous solution exerts a lævorotatory action on polarized light. The alkaline hydrates convert amygdalin into *amygdalic acid*, with evolution of ammonia; whilst on digestion with dilute hydrochloric acid, it yields glucose and *mandelic acid*. This latter compound, however, is not an immediate product, but is derived from cyanbenzylic alcohol which is first produced; and it is not improbable also that a saccharon, and not a glucose, is formed in the first instance together with the cyanbenzylic alcohol. By the action of acetic anhydride on amygdalin, seven atoms of hydrogen are displaced by the group C_2H_3O, giving rise to *heptacetylamygdalin*, $C_{20}H_{20}(C_2H_3O_2)_7NO_4$ (Schiff), a substance crystallizing in colourless silky needles; emulsin acting on amygdalin in aqueous solution causes it to split up into benzoic aldehyde, hydrocyanic acid, and a dextroglucose (comp. p. 582).

The constitution of amygdalin and of the compounds derived from it may be represented by the following formulæ:



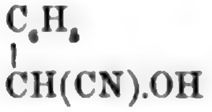
$$\begin{array}{l} C_6H_5 \\ | \\ CH(CN).O.C_{12}H_{14}O_3(OH)_7 \end{array}$$

Amygdalin.



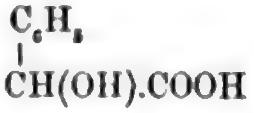
$$\begin{array}{l} C_6H_5 \\ | \\ CH(COOH).O.C_{12}H_{14}O_3(OH)_7. \end{array}$$

Amygdalic acid.



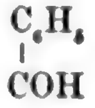
$$\begin{array}{l} C_6H_5 \\ | \\ CH(CN).OH \end{array}$$

Cyanbenzylic alcohol.



$$\begin{array}{l} C_6H_5 \\ | \\ CH(OH).COOH \end{array}$$

Mandelic acid.



$$\begin{array}{l} C_6H_5 \\ | \\ COH \end{array}$$

Benzoic aldehyde.

Apiin: (?) $C_{27}H_{32}O_{16}$.—This glucoside may be extracted from common parsley (*Apium petroselinum*) by means of boiling water. It always separates from its solutions, when they are allowed to cool slowly, as a gelatinous mass consisting of fine needles. It melts at 180° (356° F.); is soluble in boiling alcohol, but insoluble in ether. Its apparent specific rotary power in a faintly alkaline solution is (?) $[\alpha]_j = +173°$. Apiin when boiled with hydrochloric acid deposits *apigenin* in yellow flocks, which may be obtained in pearly plates by crystallization from alcohol. At the same time, a glucose is formed amounting to 41—45 per cent. of the apiin, but probably a saccharon is the immediate product of decomposition. An aqueous solution of apiin gives a blood-red colour with ferrous salts: this reaction is so delicate that it may be employed to detect the presence of very minute traces of the glucoside; ferric salts produced a brownish-red coloration.

Apigenin is perhaps represented by the formula $C_{15}H_{10}O_5$; it sublimes without melting at 292°—295° (557°·6—563° F.), but with partial decomposition. Like apiin, it is dissolved by alkalies, and also furnishes a yellow precipitate with basic plumbic acetate, but it does not reduce an alkaline solution of a copper salt. On oxidation with nitric acid, apiin yields oxalic acid and trinitrophenol; when it is fused with potassic hydrate, phloroglucol is obtained together with an acid which on further fusion with the alkali is converted into protocatechuic acid (Gerichten, *Deut. chem. Ges. Ber.*, ix. 1121).

Arbutin: $C_{25}H_{34}O_{14}$, is a colourless, bitter, crystalline substance discovered by Kawalier in the leaves of *Arctostaphylos uva ursi*, and by Zwenger and Himmelmann in the leaves of *Pyrola umbellata*. Under the influence of emulsin, or when it is boiled with dilute sulphuric acid, it is split up into quinol (hydroquinone), quinol monomethylin (methylhydroquinone), and a glucose (Hlasiwetz and Habermann, *Ann. Chem. Pharm.*, clxxvii. 339):

$$\underset{\text{Arbutin.}}{C_{25}H_{34}O_{14}} + 2OH_2 = \underset{\text{Quinol.}}{C_6H_4(OH)_2} + \underset{\text{Quinol monomethylin.}}{C_6H_4(OH).OCH_3} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

The glucose thus obtained is crystalline, and is said by Kawalier to have all the properties of sucrodextrose; its rotatory power has apparently not been determined.

Arbutin may be prepared by precipitating the aqueous decoction of the leaves with basic plumbic acetate, removing the excess of lead from the clear filtered solution by hydric sulphide, evaporating, and extracting the arbutin from the residue by a mixture of 8 parts of ether and 1 of alcohol. It crystallizes in tufts of needles which melt at 170° (338° F.); it is very sparingly soluble in ether, but easily in alcohol and in boiling water. Its aqueous solution is coloured blue by ferric chloride (Schiff). When arbutin is distilled with manganic dioxide and sulphuric acid, quinone passes over; also on passing chlorine into its aqueous solution a crystalline precipitate of a chlorinated quinone is produced. It dissolves in strong nitric acid, and the addition of alcohol to the solution causes a deposit of yellow needles consisting of *tetranitroarbutin*, $C_{25}H_{30}(NO_2)_4O_{14} + 3\frac{1}{2}OH_2$. This derivative is very soluble in water, less so in alcohol, and insoluble in ether; as already noticed (p. 526), it is said to yield dinitroquinol (dinitrohydroquinone), when boiled with dilute acids. Benzoic chloride, as also acetic chloride or acetic anhydride, act readily on arbutin, with formation of benzoyl and acetyl derivatives of arbutin apparently of the composition $C_{25}H_{24}O_{14}(C_7H_5O)_{10}$ and $C_{25}H_{24}O_{14}(C_2H_3O)_{10}$. Tetranitroarbutin also yields a corresponding acetyl derivative (Schiff, *ibid.*, cliv. 237).

On adding freshly precipitated argentic carbonate in slight excess to a solution of arbutin at a temperature of about 50° (122° F.) and heating, a solution is obtained from which—after the removal of the dissolved silver by hydrochloric acid—alcohol precipitates white crystalline flocculi of *diarbutin*, which appears to be related to arbutin in the same manner as helicoidin is to salicin; it is not coloured by ferric chloride (Schiff, *loc. cit.*).

It is difficult to assign a formula to arbutin which is in accordance with what is at present known of its properties. As it affords a blue colour with ferric chloride, and nitroarbutin is capable of forming metallic derivatives, it appears that one of the OH groups of the quinol molecule is intact, and therefore that it is derived from a saccharon as indicated by the formula:

$$C_{12}H_{14}O_4(OH)_6 \left\{ \begin{matrix} O.C_6H_4.OCH_3 \\ O.C_6H_4.OH \end{matrix} \right. ;$$

but a compound of this formula has the composition $C_{25}H_{28}O_{12}$, whilst that of arbutin is said to be $C_{25}H_{34}O_{13}$; moreover, it contains only seven OH groups, whereas, according to Schiff's analyses of the acetyl and benzoyl derivatives of arbutin it would appear that it contains at least ten OH groups.

Arnicin: $C_{20}H_{30}O_4$ (?).—A non-crystalline bitter substance extracted from the various parts of *Arnica montana*. According to Walz, it is decomposed by boiling with dilute acids, yielding dark-coloured flocks and a substance capable of reducing an alkaline solution of a cupric salt.

Aurantiin: $C_{23}H_{26}O_{12}$, a glucoside found in the flowers of *Citrus decumana*. It forms small yellow monoclinic prisms, having the composition $C_{23}H_{26}O_{12} + 4OH_2$, and melting at 171° (339°·8 F.). It has an intensely bitter taste, is very soluble in hot, but only slightly in cold water. It dissolves in alkalies, and yields a glucose when boiled with dilute acids; its aqueous solution is coloured brownish-red by ferric chloride (Hoffmann, *Deut. chem. Ges. Ber.*, ix. 690).

Bryonin: $C_{48}H_{84}O_{21}$ (?), a bitter non-crystalline compound from the root of the *Bryonia dioïca*, is decomposed by boiling with dilute acids into a glucose and two amorphous substances, *bryoretin* and *hydrobryoretin:* the former of which is soluble in ether, the latter insoluble (Walz, *Chem. Cent.*, 1859, 5):

$$(?)\ \underset{\text{Bryonin.}}{C_{48}H_{84}O_{21}} = \underset{\text{Bryoretin.}}{C_{21}H_{35}O_7} + \underset{\text{Hydrobryoretin.}}{C_{21}H_{37}O_8} + C_6H_{12}O_6.$$

Caïncin or *Caïncic acid:* $C_{40}H_{64}O_{18}$.—This substance, obtained from caïnca root, *Chiococca anguifuga* and *C. racemosa*, forms crystalline flakes, sparingly soluble in water or ether, but very soluble in alcohol. It appears to form metallic derivatives. On boiling a solution of caïncin in dilute alcohol with an acid, it is resolved into *caïncetin*, and a glucose which apparently is not sucro-dextrose:

$$\underset{\text{Caïncin.}}{C_{40}H_{64}O_{18}} + 3OH_2 = \underset{\text{Caïncetin.}}{C_{22}H_{34}O_8} + \underset{\text{Glucose.}}{3C_6H_{12}O_6}.$$

Caïncetin is indistinctly crystalline. When fused with potassic hydrate it yields butyric acid and *caïncigenin*, $C_{14}H_{24}O_2$. When treated with sodium amalgam and dilute alcohol, it dissolves to a brownish-coloured solution from which sulphuric acid throws down a crystalline substance having the composition $C_{36}H_{58}O_{15}$ (Rochleder, *Journ. pr. Chem.*, lxxxv. 275: cii. 16).

Carminic acid: $C_{17}H_{18}O_{10}$.—This substance, which is the colouring matter of cochineal, may be separated from the latter by precipitating its aqueous extract with plumbic acetate, and decomposing the washed precipitate with sulphuric acid; the solution thus obtained is alternately precipitated, and the precipitate decomposed, a second and a third time in a similar manner, employing, however, hydric sulphide to effect the final decomposition. The filtered solution is evaporated to dryness, the residue dissolved in alcohol, and the crystalline nodules of carminic acid obtained on allowing this solution to evaporate treated with water. This leaves undissolved a yellow substance, and the filtered solution after evaporation to dryness and crystallization from dry alcohol or ether, yields pure carminic acid. It also occurs in the flowers of *Monarda didyma*, and probably in other plants. Very different formulæ have been assigned to carminic acid by different chemists, and it is not improbable that it is not always of the same composition.

Carminic acid, when boiled with dilute acids, is said to be decomposed with formation of *carmine-red* and of a non-fermentable, optically inactive body, which readily reduces an alkaline solution of a cupric salt; thus:

$$(?)\ \underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + 2OH_2 = \underset{\text{Carmine-red.}}{C_{11}H_{12}O_7} + C_6H_{10}O_8.$$

Carmine-red, which may readily be prepared from the crude carminic acid obtained on decomposing by sulphuric acid the lead precipitate thrown down from a decoction of cochineal, forms a dark purple-red iridescent mass, soluble in water and in alcohol, but insoluble in ether. It forms a number of metallic derivatives, all of which are obtained as violet coloured amorphous precipitates. On oxidation with nitric acid it is converted into *trinitrocresotic acid* (*nitrococussic acid*), $CH_3.C_6H(NO_2)_3$ COOH. By treating it with concentrated sulphuric acid, a new red colouring matter, *ruficoccin*, $C_{16}H_{10}O_6$, is produced, which is probably a derivative of a hydrocarbon homologous with anthracene.

When crude carminic acid is fused with potassic hydrate and a little water, a new substance, *coccinin*, $C_{14}H_{12}O_6$ (?), is formed, together with oxalic, succinic, and apparently acetic acid. It crystallizes in yellow microscopical rectangular plates, apparently belonging to the rhombic system. They are easily soluble in alcohol, sparingly in ether, and insoluble in water, but dissolve readily in dilute alkaline solutions; the latter on exposure to the air acquires a violet and finally a purple-red colour. On passing dry ammonia over coccinin, a compound of the formula $C_{14}H_{12}O_5.NH_3$ is formed (Schaller, *Bull. Soc. Chim.* [2], ii. 414; Guignet, *ibid.*, xviii. 162; Warren De la Rue, *Chem. Soc. Memoirs*, iii. 454; Hlasiwetz and Grabowski, *Ann. Chem. Pharm.*, cxli. 329; Liebermann and Dorp, *ibid.*, clxiii. 97).

Colocynthin: $C_{56}H_{84}N_{23}$.—An intensely bitter principle, extracted from the pulp of the fruit of the bitter-apple, *Cucumis colocynthis*. It is soluble in water, alcohol, and ether; when boiled with dilute acids it yields glucose and *colocyntheïn*, a resinous substance, insoluble in water but soluble in ether:

$$\underset{\text{Colocynthin.}}{C_{56}H_{84}N_{23}} + 2OH_2 = \underset{\text{Colocynthein.}}{C_{40}H_{54}O_{13}} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

According to Walz (*Neu. Jahr. Pharm.*, ix. 225), the *alcoholic* extract of the bitter-apple contains a colourless crystalline principle, insoluble in water, which he calls *colocynthitin*.

Coniferin: $C_{16}H_{22}O_8$.—This glucoside, discovered by Rubel in the cambium of coniferous woods, has recently been investigated by Tiemann and Haarmann (*Deut. chem. Ges. Ber.*, vii. 608; viii. 509 and 1127; ix. 409). It may be obtained from the sap by boiling and filtering it to separate albumenoïd matters, concentrating to about one-fifth its volume, and allowing it to stand. The brown-coloured crystals which form are collected, pressed, and repeatedly recrystallized. Coniferin forms stellate groups of needles which have the composition $C_{16}H_{22}O_8 + 2OH_2$; they are but slightly soluble in cold water, more soluble in hot water and in alcohol, but insoluble in ether; its solutions exert a lævorotatory action on polarized light. It melts at about 185° (365° F.). If coniferin be mixed with a small quantity of phenol and concentrated sulphuric acid, an intense blue colour is produced. It does not reduce Fehling's solution, but when boiled with dilute acids it is decomposed, yielding a dextroglucose and resinous products; if, however, it be submitted to the action of emulsin at a temperature of 25°—35° (77°—95° F.), the products are dextroglucose, and a crystalline compound which may readily be separated by agitating the liquid with ether and evaporating the ethereal solution. The best method of purifying the crystalline mass thus obtained is to dissolve it in water by the aid of ammonia, and expose the solution to the air; as the ammonia evaporates the new compound, *coniferylic alcohol*, $C_{10}H_{12}O_3$, is deposited in fine, nearly colourless cystals. The decomposition of coniferin into coniferylic alcohol and dextroglucose takes place in accordance with the equation: $C_{16}H_{22}O_8 + OH_2 = C_{10}H_{12}O_3 + C_6H_{12}O_6$.

Coniferylic alcohol melts at 74°—75° (165°·2—167° F.); it is almost insoluble in cold and dissolves with difficulty in hot water; it is easily soluble in ether, less so in alcohol. It is soluble in dilute alkalies, and on allowing the solution to evaporate spontaneously, crystalline metallic derivatives containing potassium or sodium are obtained; but if the solutions are boiled down rapidly, the unaltered substance separates as an oil. If the alkaline solution be acidified, only an amorphous substance is precipitated, which appears to be a polymeride of the alcohol. On heating coniferylic alcohol with hydriodic acid, a mixture of methylic and ethylic iodides is said to be formed. When oxidized with potassic dichromate and dilute sulphuric acid it yields *vanillin* or *paroxymetamethoxybenzoic aldehyde* (methylprotocatechuic aldehyde), $C_6H_3(OH)(OCH_3)COH$, and acetic aldehyde.

Closely allied to coniferin is a substance obtained from it by oxidation with potassic permanganate, and named *glucovanillic acid*, $C_{14}H_{18}O_9$ (Tiemann and Reimer, *ibid.*, viii. 515). It crystallizes from water in slender, glistening, colourless prisms, $C_{14}H_{18}O_9 + OH_2$, which lose their water of crystallization at 100° (212° F.), and melt at 211°—212° (411°·8—413°·6 F.). It is soluble in alcohol and in hot water, but quite insoluble in ether, so that it may readily be separated from vanillic acid, which is readily soluble in ether. When heated with dilute acids or submitted to the action of emulsin, it splits up into glucose and vanillic acid, $C_6H_3(OH)(OCH_3).COOH$.

The constitution of coniferylic alcohol—and consequently of coniferin—has not yet been satisfactorily ascertained. From the formation of vanillin or oxymethoxybenzoic aldehyde on oxidation, there can be no doubt, however, that it contains the group $C_6H_3(OH)(OCH_3).C-$. Tiemann has suggested the formula $C_6H_3(OH)(OCH_3).C_3H_4(OH)$, but this does not explain the formation of ethylic iodide together with methylic iodide on heating it with hydriodic acid; moreover, a compound of this constitution should furnish acetyl derivatives, which is said not to be the case.

Convallarin: $C_{34}H_{62}O_{11}$, a colourless substance contained, together with convallamarin, in *Convallaria majalis* (Solomon's seal). It crystallizes in right rectangular prisms sparingly soluble in water. When boiled with acids it yields a glucose and *convallaretin:* $C_{34}H_{62}O_{11} + OH_2 = C_{28}H_{52}O_6 + C_6H_{12}O_6$.

Convallamarin: (?) $C_{23}H_{44}O_{12}$, a bitter substance found in *Convallaria majalis*, is a white powder, easily soluble in water or alcohol, but almost insoluble in ether. It is decomposed by dilute acids yielding *convallamaretin*, (?) $C_{20}H_{38}O_8$, and glucose.

Convolvulin: $C_{62}H_{100}O_{32}$, and *convolvulic acid:* $C_{62}H_{106}O_{34}$.—Convolvulin is a colourless, transparent resin contained in jalap root (the rhizome of *Convolvulus Schiedanus*). It is tasteless and inodorous, almost insoluble in water, easily soluble in alcohol, but insoluble in ether, whereby it is distinguished from jalapin. It dissolves in alkaline solutions, even in the cold, but far more readily when heated, being converted into a salt of *convolvulic acid*. This acid is best prepared by boiling convolvulin with baryta water, removing the baryta from the solution in the usual way, and evaporating. It is very soluble in water and in alcohol, but insoluble in ether. Both convolvulin and convolvulinic acid are decomposed by boiling with dilute acids, yielding *convolvulinol*, $C_{26}H_{50}O_7$, and a glucose the nature of which is undetermined:

$$C_{62}H_{100}O_{32} + 11OH_2 = C_{26}H_{50}O_7 + 6C_6H_{12}O_6.$$

The former dissolves in alkalies, but not in water, and on the addition of an acid convolvulinolic acid, $C_{13}H_{24}O_4$, separates from the solution in microscopic needles which melt at 39° (102°·2 F.). It is easily soluble in alcohol, less so in ether. According to Mayer (*Ann. Chem. Pharm.*, xcvi. 61), the substances obtained in this way from convolvulin and convolvulic acid are not identical, but the whole subject requires careful re-examination. On oxidation with nitric acid, convolvulin and its derivatives are converted into *ipomæic acid* (*sebacic acid*), $C_{10}H_{18}O_4$, an acid of the succinic series (comp. Neison and Bayne, *Journ. Chem. Soc.*, 1874, xxvii. 729).

Crocin: $C_{58}H_{84}O_{30}$, the colouring matter of *Gardenia grandiflora*, is an amorphous red substance, easily soluble in water and in alcohol with a deep yellow colour. The solutions yield an orange-coloured precipitate with plumbic salts. Boiled with dilute acids, crocin is resolved into *crocetin*, $C_{34}H_{46}O_{11}$, and an uncrystallizable glucose: $C_{58}H_{84}O_{30} + 5OH_2 = C_{34}H_{46}O_{11} + 4C_6H_{12}O_6$.

Crocetin is a dark red amorphous powder easily soluble in alcohol, but only slightly in water. Like crocin it becomes indigo blue, and finally violet, when treated with concentrated sulphuric acid (Rochleder, *Jour. pr. Chem.*, lvi. 68).

Cyclamin: $C_{20}H_{34}O_{10}$, a white amorphous substance extracted from the tubers of *Cyclamen europæum* by means of alcohol. It is readily soluble in hot alcohol, but insoluble in ether. In contact with cold water it swells up to a translucent glutinous substance which slowly dissolves. The liquid froths when agitated, and possesses a feeble lævorotatory action. When boiled with dilute acids it yields *cyclamiretin* and glucose (?): $C_{20}H_{34}O_{10} + 2OH_2 = C_{14}H_{26}O_6 + C_6H_{12}O_6$.

Daphnin: $C_{15}H_{16}O_9$ (?), a colourless glucoside contained in the bark of various species of *Daphne*. It crystallizes in transparent rectangular prisms which are insoluble in ether, sparingly soluble in cold water, but more freely in warm water, and still more so in alcohol. It fuses at about 200° (392° F.). According to Rochleder (*Jahresb*, 1863, 591), daphnin is isomeric or polymeric with æsculin. On boiling with dilute acids, or on treatment with emulsin, it yields glucose and *daphnetin*, $C_9H_8O_5$ (?), isomeric with hydrated æsculetin: $C_{15}H_{16}O_9 + 2OH_2 = C_9H_8O_5 + C_6H_{12}O_6$. Daphnetin crystallizes in small, needle-shaped, monoclinic prisms, which are easily soluble in alcohol and in boiling water, but only sparingly in ether. It fuses above 250° (482° F.), and may readily be sublimed in a current of gas.

Datiscin: $C_{21}H_{22}O_{12}$.—This glucoside obtained from the leaves and roots of *Datisca cannabina*, crystallizes in silky needles which are sparingly soluble in cold water, very soluble in hot alcohol, but only slightly in ether. It melts at 180° C. (356° F.). When boiled with dilute acids, or with a concentrated solution of potassic hydrate, it is decomposed with formation of glucose and *datiscetin:* $C_{21}H_{22}O_{12} = C_{15}H_{10}O_6 + C_6H_{12}O_6$. This change is not effected by yeast or by emulsin. Datiscetin crystallizes easily in long needles, which are almost insoluble in water, but readily in alcohol or ether. When heated with nitric acid, it yields trinitrophenol but no oxalic acid. Both datiscin and datiscetin give precipitates with lead acetate.

Digitalin.—This, the active principle of the foxglove, *Digitalis purpurea*, has been examined by numerous investigators, but the results hitherto obtained have been anything but satisfactory or concordant. According to Nativelle (*Jour. Pharm.* [4], xx. 81), a crystalline compound may be obtained from digitalis extract after treating it with lead acetate and a little water, by a long and tedious process. Lefort (*ibid.* [5], vi. 424) exhausts the leaves with dilute alcohol, precipitates with basic lead acetate, removes the excess of lead from the solution by sodic carbonate, and then precipitates the digitalin by tannin. The brown precipitate after being thoroughly washed is decomposed by digesting it with finely-powdered plumbic oxide and treated with alcohol. The solution, after decoloration with animal charcoal, yields crystallized digitalin on evaporation, whilst the more soluble modification remains in solution. This author attributes the discrepancies in the statements respecting digitalin to the existence of two modifications of this body, one more soluble obtained from the seeds, the other less soluble crystallized variety predominating in the leaves. Crystallized digitalin forms microscopic plates, which are inodorous and possess a very persistent bitter taste. It is almost insoluble in ether, very soluble in chloroform, and requires about ten parts of alcohol at ordinary temperatures. Its most characteristic reaction is the beautiful green colour it assumes when treated with a very concentrated solution of phosphoric acid.

The formula of digitalin is still a matter of doubt. According to Kosmann (*ibid.* [4], xx. 427), both the soluble and insoluble forms of digitalin are glucosides; the first yielding four molecules of glucose, and being easily transformed by the action of saline or acid agents into the insoluble form, which yields but two molecules of glucose:

$$\underset{\text{Soluble digitalin.}}{C_{54}H_{84}O_{27}} + 3OH_2 = \underset{\text{Insoluble digitalin.}}{C_{42}H_{66}O_{18}} + 2C_6H_{12}O_6;$$

$$\underset{\text{Insoluble digitalin.}}{C_{42}H_{66}O_{18}} + 4OH_2 = \underset{\text{Digitaliretin.}}{C_{30}H_{50}O_{10}} + 2C_6H_{12}O_6.$$

Digitaliretin forms shining plates which melt at 169° (336°·2 F.). It is almost insoluble in water, sparingly soluble in ether or cold alcohol, but readily in boiling alcohol (comp. Schmiedeberg, *Pharm. J. Trans.* [3], v. 741). Kosmann, by boiling digitalin with a dilute alkaline solution and precipitating by an acid, obtained *digitalic acid*, $C_{54}H_{96}O_{33}$, a substance crystallizing from alcohol, and capable of forming crystalline salts. By boiling with acids it is resolved into digitaliretin and glucose.

Dulcamarin: $C_{22}H_{34}O_{10}$.—Geissler (*Arch. Pharm.* [3], vii. 289) has recently examined the supposed alkaloïd from *Solanum dulcamara*, and finds that it consists of two substances separable by ammonia. The solution contains the dulcamarin, which may be obtained as a pale yellow powder having a bitter taste. It is soluble in acetic acid, but insoluble in ether, chloroform, and benzene. It is unaffected by emulsin, but boiling with dilute sulphuric acid causes it to split up into *dulcamaretin* and glucose: $C_{22}H_{34}O_{10} + 2OH_2 = C_{16}H_{26}O_6 + C_6H_{12}O_6$. Dulcamaretin is precipitated as a tarry product, insoluble in ether, chloroform, and benzene, but soluble in alcohol. After purification it forms a brownish-black resinous body destitute of odour and taste.

Ericolin: $C_{34}H_{56}O_{21}$.—This compound exists in several plants of the order *Ericaceæ*, and especially in the marsh rosemary, *Ledum palustre*. It is a resinous substance, soluble in alcohol, but only slightly soluble in water. When boiled with dilute acids it yields glucose and *ericinol*: $C_{34}H_{56}O_{21} + 4OH_2 = C_{10}H_{16}O + 4C_6H_{12}O_6$. Ericinol is a volatile colourless oil, which turns brown on exposure to the air. It boils at 240°—242° (464°—467°·6 F.), and has a disagreeable odour and nauseous burning bitter taste. It has a specific gravity of 0·874° at 20° (68° F.).

Frangulin: (?) $C_{20}H_{20}O_{10}$.—Frangulin may be obtained from the bark of *Rhamnus frangula* by fractionally precipitating the alcoholic extract with normal and basic plumbic acetate, suspending the final precipitate in alcohol and decomposing it with sulphuretted hydrogen. The solution boiled and filtered deposits the substance in a crystalline state on cooling. It forms a yellow silky crystalline mass melting at 226° (438°·8 F.) (Faust, *Ann. Chem. Pharm.*, clxv. 231), insoluble in water, and only slightly soluble in cold alcohol or boiling ether. When boiled with dilute acids it splits up into glucose and *frangulic acid*, (?) $C_{14}H_8O_4$. Liebermann and Waldstein (*Deut. chem. Ges. Ber.*, ix. 1075) suggest the formula $C_{21}H_{20}O_{10}$ for frangulin, and $C_{15}H_{10}O_5$ for frangulic acid, which is apparently a derivative either of anthracene or of methylanthracene.

Fraxin or *Paviin*: $C_{16}H_{18}O_{10}$.—A fluorescent substance existing in the bark of the ash, *Fraxinus excelsior*, and along with æsculin in the horse chestnut. It crystallizes in tufts of colourless needles, having the composition $2C_{16}H_{18}O_{10} + OH_2$. These lose their water of crystallization when heated in a stream of carbonic anhydride at 150° (302° F.). Fraxin melts at 190° (374° F.). It is but sparingly soluble in cold water or alcohol, but comparatively easily when hot. It is more soluble in ether than æsculin. Fraxin exhibits a strong green-blue fluorescence which is increased by alkalies, but destroyed by acids. Boiled with dilute acids, it is resolved into glucose and *fraxetin*: $C_{16}H_{18}O_{10} + OH_2 = C_{10}H_8O_5 + C_6H_{12}O_6$. Fraxetin forms colourless needles which are almost insoluble in water, but somewhat more so in alcohol.

Globularin: (?) $C_{30}H_{44}O_{14}$.—A glucoside existing, according to Walz, in the leaves of *Globularia alypum*, and which, when boiled with dilute acids, is resolved into glucose, *globularetin*, $C_{12}H_{14}O_3$, and *paraglobularetin*, $C_{12}H_{16}O_4$, both amorphous substances.

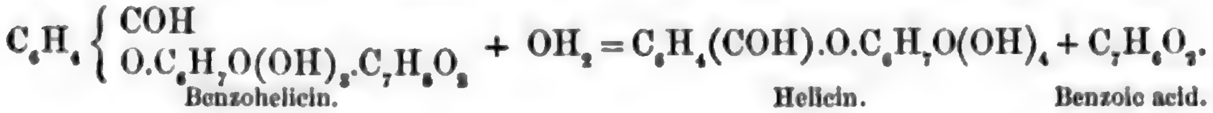
Glycyrrhizin: (?) $C_{24}H_{36}O_9$. is a substance of sweet taste obtained from the liquorice root, *Glycyrrhiza glabra* and *G. echinata*; it crystallizes from glacial acetic acid in aggregates of almost colourless prismatic needles; easily soluble in hot water or in alcohol, but only sparingly soluble in cold water. Its aqueous solution is precipitated by salts of barium, magnesium, and copper, and by basic plumbic acetate. When boiled with dilute acids, glycyrrhizin is resolved into glucose and *glycyrretin*, (?) $C_{18}H_{26}O_4$. Glycyrretin is a brownish-yellow resinous substance, insoluble in water, but soluble in alcohol and in alkaline solutions (Habermann, *Deut. chem. Ges. Ber.*, x. 870).

Gratiolin: (?) $C_{40}H_{64}O_{14}$, and *Gratiosolin*: (?) $C_{46}H_{84}O_{25}$.—Two amorphous glucosides contained in the *Gratiola officinalis*. When boiled with a dilute acid the first is said to yield *gratioletin*, $C_{17}H_{28}O_3$, a crystallizable substance, and an amorphous compound, *gratioleretin*, $C_{17}H_{28}O_3$, besides a glucose. Gratiosolin, under similar circumstances, yields glucose and *gratiosoletin*, $C_{40}H_{68}O_{17}$, the latter being resolved by continued boiling with acids into a mixture of *gratiosoleretin*, $C_{34}H_{52}O_9$, and *hydrogratiosoleretin*, $C_{34}H_{56}O_{11}$.

Helicin: $C_{13}H_{16}O_7$.—The glucoside of salicylic aldehyde obtained by treating salicin with very dilute nitric acid:

$$\underset{\text{Salicin.}}{C_6H_4(CH_2.OH).O.C_6H_7O(OH)_4} + O = \underset{\text{Helicin.}}{C_6H_4(COH).O.C_6H_7O(OH)_4} + OH_2;$$

And also from benzohelicin by boiling it with magnesia and water, when it splits up into benzoic acid and helicin:



$$\underset{\text{Benzohelicin.}}{C_6H_4\left\{\begin{matrix}COH\\O.C_6H_7O(OH)_3.C_7H_5O_2\end{matrix}\right.} + OH_2 = \underset{\text{Helicin.}}{C_6H_4(COH).O.C_6H_7O(OH)_4} + \underset{\text{Benzoic acid.}}{C_7H_6O_2}.$$

It forms very slender needles, which are insoluble in ether, sparingly soluble in cold water, but freely in hot water or in alcohol. It melts at 175° (347° F.), and when submitted to the action of emulsin or boiled with dilute acids, it yields glucose and salicylic aldehyde:

$$C_6H_4(COH).O.C_6H_7O(OH)_4 + OH_2 = C_6H_4(OH).COH + C_6H_7O(OH)_5.$$

By the action of bromine or chlorine, helicin is converted into *monobromhelicin* and *monochlorhelicin* respectively, the latter of which exists in two isomeric modifications. When helicin in aqueous solution is treated with sodium amalgam, the nascent hydrogen reconverts it into salicin. With acetic chloride it yields *tetracetylhelicin*, $C_{13}H_{12}(C_2H_3O)_4O_7$ (Schiff, *Ann. Chem. Pharm.*, cliv. 1).

Benzohelicin: $C_{20}H_{20}O_8$.—This compound may be produced synthetically by treating helicin with benzoic chloride, C_7H_5OCl., at 60° (140° F.), whilst at 150° (302° F.) with excess of the chloride it yields *tetrabenzoylhelicin*, $C_{13}H_{12}(C_7H_5O)_4O_7$ (Schiff). Benzohelisin may also be prepared from benzoylsalicin or populin in a manner similar to that employed in preparing helicin from salicin. It crystallizes in tufts of silky needles which are soluble in boiling water. It is not altered by emulsin, but acids or alkalies decompose it readily, thus:

$$\underset{\text{Benzohelicin.}}{C_6H_4\left\{\begin{matrix}COH\\ O.C_6H_7O(OH)_3(O.C_7H_5O)\end{matrix}\right.}+2OH_2=\underset{\text{Salicylic aldehyde.}}{C_6H_4(OH).COH}+\underset{\text{Benzoic acid.}}{C_7H_6O_2}+\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

Helicoïdin: $C_{26}H_{34}O_{14}$.—This substance is formed by the action of very dilute nitric acid on salicin: $2C_{13}H_{18}O_7+O=C_{26}H_{34}O_{14}+OH_2$. and also when a solution of helicin is treated with sodium amalgam; being converted, however, into salicin by the continued action of nascent hydrogen. Under the influence of emulsin it is resolved into saligenol, $C_7H_8O_2$, salicylic aldehyde and glucose:

$$\left.\begin{matrix}C_6H_4[O.C_6H_7O(OH)_4].CH_2.O\\ C_6H_4[O.C_6H_7O(OH)_4]CH.OH\end{matrix}\right\}+2OH_2-C_6H_4(OH).CH_2.OH+C_6H_4(OH)COH+2C_6H_{12}O_6.$$

If the formula here assigned to helicoïdin be correct, it should furnish a nonacetyl derivative and not an octacetyl derivative (comp. Schiff, *loc. cit*).

Helleborin: $C_{36}H_{42}O_6$, and *Helleboreïn:* $C_{26}H_{44}O_{15}$, are two glucosides existing in the roots of *Helleborus niger* and *H. viridis*. Helleboreïn is much more abundant in black than in green hellebore, but always occurs in larger quantity than helleborin, which should be prepared from green hellebore, as it occurs very sparingly in the black. *Helleborin* forms glistening white needles, insoluble in cold water, easily soluble in boiling alcohol and in chloroform. It is a stronger narcotic than helleboreïn, and when boiled with dilute acids, it is resolved into glucose and *helleboresin*, $C_{30}H_{38}O_4$, a resinous substance insoluble in water, but easily soluble in boiling alcohol: $C_{36}H_{42}O_6+4OH_2=C_{30}H_{38}O_4+C_6H_{12}O_6$. *Helleboreïn* may be obtained from its alcoholic solution in nodular masses consisting of microscopic needles: it is very soluble in water, less so in alcohol, and insoluble in ether. Boiling dilute acids resolve it into glucose and *helleboretin*, which is thrown down as a dark violet-blue precipitate: $C_{26}H_{44}O_{15}=C_{14}H_{20}O_3+2C_6H_{12}O_6$. Helleboretin forms a greyish-green amorphous and tasteless powder, which melts above 200° (392° F.), and is insoluble in water and ether, but easily soluble in alcohol, yielding a violet-coloured solution (Husemann and Marmé, *Ann. Chem. Pharm.*, cxxxv. 55).

Hesperidin: $C_{22}H_{26}O_{12}$, is most easily prepared from unripe bitter oranges by exhausting them with water, treating the residue with a mixture of equal parts of water and alcohol containing 1 per cent. of potassic hydrate, and precipitating the impure hesperidin from the clear solution by hydrochloric acid. When pure, it forms microscopic needles which are almost insoluble in cold water, more soluble in alcohol and hot acetic acid, and easily soluble in ammonia; it is insoluble in ether and benzene, and melts at about 245° (473° F.). When hesperidin is boiled with dilute acids, it is resolved into glucose and *hesperetin:* $C_{22}H_{26}O_{12}=C_{16}H_{14}O_6+C_6H_{12}O_6$. Hesperetin forms colourless crystals, having a sweet taste and melting at 223° (433°·4 F.). It is almost insoluble in cold water, but dissolves readily in alcohol or ether, and in alkalies; the aqueous solution is coloured brown-red by ferric chloride. When heated with potassic hydrate solution at 100° (212° F.), it is resolved into phloroglucol and *hesperitic acid:* $C_6H_{14}O_6+OH_2=C_{10}H_{10}O_4+C_6H_3(OH)_3$; but when hesperetic acid or hesperetin is fused with potassic hydrate, protocatechuic acid is obtained. It is probable that hesperetin is related to coniferylic alcohol, as on heating it with water at 250° (482° F.) a substance smelling strongly of vanilla is produced (Hilger, *Deut. chem. Ges. Ber.*, ix. 26; Hofmann, *ibid.*, ix. 685; Paterno and Briosi, *ibid.*, ix. 250).

Jalapin or *Scammonin:* $C_{34}H_{56}O_{16}$, and *Jalapic Acid:* $C_{34}H_{60}O_{18}$ (?).—Jalapin is a glucoside occurring in the root stalk of *Convolvulus Orizabensis*, and may be prepared from commercial *Resina jalappæ ex stipitibus* or from scammony resin (from *C. scammonia*). It is a colourless amorphous resin, only slightly soluble in water, but freely in alcohol, ether, and chloroform. Jalapin from jalap when heated with dilute acids is resolved into glucose and *jalapinol* (Mayer, *Ann. Chem. Pharm.*, xcv. 129): $2C_{34}H_{56}O_{16} + 11OH_2 = C_{32}H_{62}O_7 + 6C_6H_{12}O_6$; whilst according to Spirgatis (*ibid.*, cxvi. 289), the jalapin from scammony yields glucose and *jalapinolic acid*: $C_{34}H_{56}O_{16} + 5OH_2 = C_{16}H_{30}O_3 + 3C_6H_{12}O_6$.

Jalapinol forms white dendritic crystalline masses, which are soluble in alcohol and ether, and melt at 62° (143°·6 F.). In contact with alkaline solutions, ammonia, or baryta, it is converted into a salt of jalapinolic acid: $C_{32}H_{62}O_7 + BaH_2O_2 = (C_{16}H_{29}O_3)_2Ba + 3OH_2$.

Jalapinolic acid crystallizes in tufts of colourless needles which melt at 64° (147°·2 F.). It is insoluble in water, but soluble in alcohol or ether. It is a monobasic acid, and forms crystalline salts with the metals of the alkalies, with ammonia, and with barium; the compounds with the heavy metals are mostly amorphous. When oxidized with nitric acid it yields sebacic acid (comp. convolvulin).

Jalapic acid, or *scammonic acid*, an amorphous yellowish brittle substance very soluble in water or alcohol, but less so in ether, is formed from jalapin by the assimilation of water. It is prepared by boiling jalapin with baryta water until dissolved, removing the baryta in the usual way, and evaporating. By the action of concentrated hydrochloric acid it is resolved into jalapinol and glucose (Mayer): $2C_{34}H_{60}O_{18} + 7OH_2 = C_{32}H_{62}O_7 + 6C_6H_{12}O_6$. Sometimes when jalapic acid is boiled for a short time with hydrochloric acid a compound *alphajalapic acid*, $C_{28}H_{50}O_{13}$, is produced, intermediate between jalapinol and jalapic acid; it is probably formed from the latter by the elimination of a molecule of glucose: $C_{34}H_{60}O_{18} + OH_2 = C_{28}H_{50}O_{13} + C_6H_{12}O_6$. It crystallizes in silky needles which melt below 80° (176° F.). Dilute acids convert it into jalapinol and glucose: $2C_{28}H_{50}O_{13} + 5OH_2 = C_{32}H_{62}O_7 + 4C_6H_{12}O_6$.

Menyanthin: (?) $C_{30}H_{46}O_{14}$.—A bitter amorphous substance discovered by Brandes in the buckbean, *Menyanthes trifoliata*. It is insoluble in ether, sparingly soluble in cold water, but more readily in hot water or in alcohol. When distilled with dilute sulphuric acid it is decomposed, a colourless, oil *menyanthol*, C_8H_8O (?), passing over, having an odour similar to benzoic aldehyde, whilst dextroglucose remains behind (Kromayer, *Arch. Pharm.* [2], cxxiv. 37).

Murrayin: $C_{36}H_{44}O_{20}$, a glucoside obtained by De Vrij from *Murraya exotica*, crystallizes in minute needles, which have a slightly bitter taste. It melts at 170° (338° F.), is insoluble in ether, sparingly soluble in cold water, but easily in boiling water or in alcohol. The crystals have the formula, $C_{36}H_{44}O_{20} + OH_2$, but lose their water of crystallization at 115° (239° F.). Heated with dilute acids it is resolved into *murrayetin* and glucose: $C_{36}H_{44}O_{20} + 2OH_2 = C_{24}H_{24}O_{10} + 2C_6H_{12}O_6$. Murrayetin crystallizes in silky needles or in rhombic prisms. It is only slightly soluble in cold water, but easily in alcohol. Both murrayin and murrayetin are fluorescent in alkaline solution (Blas, *Zeits. Chem.*, v. 316; Hoffmann, *Deut. chem. Ges. Ber.*, ix. 690).

Myronic acid: $C_{10}H_{19}NS_2O_{10}$.—The potassium salt of this acid occurs in the seed of the black mustard, *Sinapis nigra*, and may be obtained by crystallization from alcohol in silky needles, whilst from its aqueous solution it separates in short transparent rhombic prisms. It is easily soluble in water, but only with difficulty in alcohol. When a dilute solution is submitted to the action of *myrosin*, an albumenoid substance contained in *white* mustard, it is readily decomposed, yielding allylic thiocyanate, C_3H_5NCS, and glucose (comp. p. 582):

$$C_{10}H_{18}KNS_2O_{10} = C_3H_5NCS + C_6H_{12}O_6 + KHSO_4.$$

Potassic myronate is not decomposed by emulsin or by yeast. Free myronic acid may be obtained from the crystalline barium compound by decomposing it with dilute sulphuric acid. The solution of the acid dries up to an uncrystallizable syrup, which is soluble in alcohol but not in ether.

Ononin: (?) $C_{62}H_{68}O_{27}$, and *Onospin:* (?) $C_{60}H_{68}O_{25}$.—Ononin, a compound existing in the root of *Ononis spinosa*, may be obtained in colourless needles, which melt at 235° (455° F.). It is but sparingly soluble in boiling water, more so in boiling alcohol, and insoluble in ether. When boiled with a solution of an alkali, or with baryta water, it yields *onospin* and a formate: $C_{62}H_{68}O_{27} + 2OH_2 = C_{60}H_{68}O_{25} + 2H.COOH$. Hydrochloric or dilute sulphuric acid, when heated with ononin, decompose it with formation of *formonetin*, $C_{50}H_{40}O_{13}$, and glucose: $C_{62}H_{68}O_{27} = C_{50}H_{40}O_{13} + 2C_6H_{12}O_6 + 2OH_2$. Formonetin forms colourless crystals, which are nearly insoluble in water and in ether, but somewhat soluble in alcohol.

Onospin is deposited from its boiling aqueous solution as a white crystalline mass. It is insoluble in ether, but easily soluble in alcohol, and in alkaline solutions, being precipitated from the latter on the addition of an acid. It melts at 162° (323°·6 F.), and when boiled with dilute acids yields *ononetin*, $C_{48}H_{44}O_{13}$, and glucose: $C_{60}H_{68}O_{25} = C_{48}H_{44}O_{13} + 2C_6H_{12}O_6$. Ononetin may also be obtained by decomposing formonetin by boiling it with baryta water: $C_{50}H_{40}O_{13} + 4OH_2 = C_{48}H_{44}O_{13} + 2H.COOH$. Ononetin crystallizes in long colourless prisms, which melt at 120° (248° F.). It is nearly insoluble in water, but soluble in alcohol and in alkaline solutions. Its ammoniacal solution when exposed to the air acquires a deep green colour (Hlasiwetz, *Wien. Akad. Ber.*, xv. 142).

Paridin: $C_{32}H_{56}O_{14}$ (?) and *Paristyphnin:* $C_{38}H_{64}O_{18}$ (?), two glucosides contained in *Paris quadrifolia*. Paridin crystallizes in thin plates, or in tufts of needles. It is only slightly soluble either in boiling water or alcohol, and when boiled with hydrochloric acid in dilute alcoholic solution yields *paridol*, $C_{26}H_{46}O_9$, and glucose: $C_{32}H_{56}O_{14} + OH_2 = C_{26}H_{46}O_9 + C_6H_{12}O_6$. Paristyphnin is an amorphous substance which, when boiled with water, yields glucose and paridin: $C_{38}H_{64}O_{18} + 2OH_2 = C_{32}H_{46}O_9 + C_6H_{12}O_6$.

Phillyrin: $C_{27}H_{34}O_{11}$, a colourless crystalline substance extracted from the bark of *Phillyrea latifolia*. It has a bitter taste, is but sparingly soluble in cold water, more so in boiling water and in alcohol, but insoluble in ether. It melts at 160° (320° F.), and when boiled with dilute hydrochloric acid, it is resolved into phillygenin, and a glucose: $C_{27}H_{34}O_{11} + OH_2 = C_{21}H_{24}O_6 + C_6H_{12}O_6$. *Phillygenin* may be obtained in a nacreous mass of crystals which are almost insoluble in cold water, but dissolve readily in alcohol or ether. Both phillyrin and phillygenin yield substitution compounds by the action of chlorine, bromine, and nitric acid.

Phlorizin and *Isophlorizin:* $C_{21}H_{24}O_{10}$.—Phlorizin is found in the root bark of the apple, pear, plum, and cherry tree, and may readily be extracted by treating the bark with dilute alcohol, decolorizing the solution with animal charcoal, and concentrating. It crystallizes in slender silky needles, which are only sparingly soluble in cold water, but readily on boiling. It is also easily soluble in alcohol, but insoluble in ether. The crystals have the composition $C_{21}H_{24}O_{10} + 2OH_2$, but lose their water at 100° (212° F.). Anhydrous phlorizin melts at 109° (228°·2 F.). By the simultaneous action of air and ammonia on phlorizin, an uncrystallizable reddish-brown product is obtained, called *phlorozeïn*, having the composition $C_{21}H_{30}N_2O_{13}$. By boiling phlorizin for a short time with dilute acids, or by prolonged contact in the cold, it is decomposed into phloretin and a glucose (comp. p. 582): $C_{21}H_{24}O_{10} + OH_2 = C_{15}H_{14}O_5 + C_6H_{12}O_6$. *Phloretin* crystallizes in microscopic plates almost insoluble in cold, and but sparingly soluble even in boiling water or in ether; very soluble in hot alcohol.

It melts at 180° (356° F.). It yields bromo- and nitro-derivatives by the action of bromine and of nitric acid respectively. *Tetrabromophloretin*, $C_{15}H_{10}Br_4O_5$, crystallizes in pale yellow needles, which melt at 205°—210° (401°—410° F.). It is insoluble in water, sparingly soluble in alcohol, but easily soluble in ether. *Nitrophloretin*, $C_{15}H_{13}(NO_2)O_5$, is a brown amorphous compound.

When phloretin is boiled for some time with a concentrated solution of potassic hydrate, it is decomposed, yielding *phloretic acid* (comp. p. 493), $C_9H_{10}O_3$, and phloroglucol, $C_6H_6O_3$.

Isophlorizin, according to Rochleder (*Zeits. Chem.*, iv. 721), occurs in the leaves of the apple-tree. It crystallizes in thin silvery needles, which melt at 105° (221° F.). Dilute acids act on it far more readily than on phlorizin, giving rise to *isophloretin* and a glucose. Isophloretin closely resembles phloretin, but is easily soluble in ether. By the action of potassic hydrate, it yields phloroglucol and *isophloretic acid*.

Pinipicrin: $C_{22}H_{36}O_{11}$, a bitter glucoside occurring in the needles and bark of the Scotch fir (*Pinus Sylvestris*) and in the *Thuja occidentalis*, forms a bright yellow powder, which melts at about 100° (212° F.). It is soluble in alcohol, very soluble in water, but insoluble in pure dry ether. When heated with dilute acids, it is resolved into *ericinol* and a glucose: $C_{22}H_{36}O_{11} + 2OH_2 = C_{10}H_{16}O + 2C_6H_{12}O_6$.

Populin or *Benzoylsalicin:* $C_{20}H_{22}O_8$, was discovered by Braconnot, in the bark and leaves of the aspen (*Populus tremula*). It crystallizes in colourless, silky needles of the composition $C_{20}H_{22}O_8 + 2OH_2$, which part with their water below 100° (212° F.). Anhydrous populin melts at 180° (356° F.). Populin dissolves in 70 pts. boiling water, but is only slightly soluble in the cold. It is more soluble in alcohol, but almost insoluble in ether. Dilute nitric acid oxidizes it to *benzohelicin*, $C_{20}H_{20}O_8$ (*vide* Helicin), but when boiled with dilute sulphuric or hydrochloric acid, it is converted into glucose, benzoic acid, and saligenol, $C_7H_8O_2$:

$$C_6H_4\left\{\begin{matrix}O.C_6H_7O(OH)_3(C_7H_5O_2)\\CH_2.OH\end{matrix}\right.+2OH_2=C_6H_{12}O_6+C_6H_5.COOH+C_6H_4(OH).CH_2.OH$$

—but the saligenol is converted into saliretin by the further action of the acid. Boiled with baric or calcic hydrate, it yields salicin and benzoic acid: $C_{20}H_{22}O_8 + OH_2 = C_{13}H_{18}O_7 + C_7H_6O_2$. Emulsin has no action on populin.

Prophetin: $C_{22}H_{36}O_7$, a bitter, resinous principle contained in the fruit of *Cucumis prophetarum*, which when boiled with acids yields *propheterin*, $C_{20}H_{30}O_4$, and a substance of the nature of glucose.

Quinovin or *Quinova bitter:* $C_{30}H_{48}O_8$, is found in the false cinchona bark (*Cinchona nova*), and according to De Vrij in the *C. Calisaya* of Java. It is an amorphous substance possessing a very bitter taste, almost insoluble in water, very soluble in alcohol, and moderately so in ether and chloroform. It is dextrorotatory, but is less active than quinovic acid. By passing dry hydrochloric acid into an alcoholic solution of quinovin, it is resolved into *quinovic acid*, $C_{24}H_{38}O_4$, and a peculiar saccharine substance called *quinova-sugar:* $C_{30}H_{48}O_8 + OH_2 = C_{24}H_{38}O_4 + C_6H_{12}O_5$. The quinovic acid, which is deposited as a white crystalline powder consisting of minute six-sided plates, is insoluble in water, and only sparingly soluble in ether or boiling alcohol. It is dibasic, and only possesses feeble acid properties, but is capable of decomposing the alkaline carbonates. Its salts are not crystalline.

Quinovatannic acid, a substance resembling quinotannic acid, obtained by Hlasiwetz (*Ann. Chem. Pharm.*, lxxix. 130) from the bark of *Cinchona nova* and *C. surinamensis*. It does not yield any precipitate either with gelatin or with tartar emetic, and when boiled with dilute acids, it is decomposed with formation of cinchona-red, and a saccharine substance.

Ratanhia-tannic acid, a peculiar tannin found in the bark of rhatany-root, ***Krameria triandra***, which when boiled with dilute sulphuric acid yields *ratanhia-red*, $C_{28}H_{22}O_{11}$, and a difficultly-crystallizable glucose. On being fused with potassic hydrate. ratanhia-red is resolved into protocatechuic acid and phloroglucol.

Rhamnin and ***Rhamnegin***, ***Xanthorhamnin***, ***Chrysorhamnin*** : $C_{24}H_{32}O_{14}$. The yellow colouring matters contained in "Persian berries," or "*graines d'Avignon*," derived from the *Rhamnus amygdalinus*, *R. oleoides*, *R. saxatilis*, growing in Persia and Turkey, and the *R. infectorius* and *R. tinctorius*, growing in Avignon, have been examined by many investigators, but the results obtained are somewhat conflicting, and the nature and composition of these compounds cannot be regarded as definitely settled.

According to Lefort (*Compt. Rend.*, lxiii. 840, and lxvii. 345), there are two isomeric substances present in the fruits, one of which, *rhamnin*, is amorphous and insoluble in water, but soluble in boiling alcohol; the other, *rhamnegin*, crystallizes in tufts of minute needles of a yellowish-white colour, easily soluble in water and in hot alcohol. It appears to be identical with the *xanthorhamnin* of Gellatly. Rhamnegin when boiled with very dilute acids is completely converted into the isomeric rhamnin, which by the action of stronger acids yields *rhamnetin*, $C_{12}H_{10}O_5$, and an isomeride of mannitol (?): $C_{24}H_{32}O_{14} + 3OH_2 = C_{12}H_{10}O_5 + 2C_6H_{14}O_6$. Rhamnetin is a pale yellow, crystalline substance, very similar in properties to quercetin, with which it is considered to be identical by Hlasiwetz (*Ann. Chem. Pharm.*, cxii. 107) and by Stein (*Zeits. chem.*, v. 183, 568). When fused with potassic hydrate, it yields phloroglucol and quercetic acid. Schützenberger states (*Compt. Rend.*, lxix. 350) that rhamnegin may be formed synthetically from rhamnetin by heating its lead compound with diacetylsaccharon at 140° (284° F.).

The berries of the buckthorn, *R. catharticus*, contain *rhamnegin*, or, according to Schützenberger, two isomeric modifications of rhamnegin, one of which is more soluble in alcohol than the other, and also more fusible.

Rhinanthin : $C_{29}H_{52}O_{20}$, a glucoside contained in the seeds of the yellow rattle, *Rhinanthus Crista Galli*, and in those of *Alectrolophus hirsutus*, crystallizes in stellate groups of prisms which are easily soluble in water and in alcohol. It is decomposed by acids yielding a saccharine substance and a brown non-crystalline compound, *rhamnogenin*.

Robinin ; $C_{25}H_{30}O_{16}$, a yellow crystalline glucoside obtained from the blossoms of the *Robinia pseudacacia*. It forms silky needles which lose their water of crystallization at 100°. Robinin melts at 195° (383° F.). It is insoluble in ether, and but slightly soluble in cold water or alcohol. When boiled with dilute acids, it is said to split up in the manner indicated in the equation: $C_{25}H_{30}O_{16} + 2OH_2 = C_{12}H_{10}O_6 + 2C_6H_{12}O_6$, yielding quercetin and a peculiar species of sugar, *robinin-sugar*, which does not crystallize, and which when heated with nitric acid yields trinitrophenol and traces of oxalic acid. It does not undergo fermentation in contact with yeast.

Rutin, ***Phylometin***, or ***Melin*** : $C_{25}H_{28}O_{15},2OH_2$, is a glucoside which appears to be very widely diffused in the vegetable kingdom, being contained in garden rue, *Ruta graveolens*, in capers, from *Capparis spinosa*, and in "*Waifa*" or Chinese yellow, in grains, the undeveloped flower buds of *Sophora japonica*. It crystallizes from its aqueous solution in pale yellow slender needles, which lose their water of crystallization at 150° (302° F.). It is insoluble in ether, only slightly soluble in cold water or alcohol, but readily on boiling. It also dissolves easily in dilute alkaline solutions. When boiled with dilute acids, it yields quercetin and a glucose: $C_{25}H_{28}O_{15} + 3OH_2 = C_{12}H_{10}O_6 + 2C_6H_{12}O_6$. The glucose forms a colourless uncrystallizable syrup which yields oxalic acid when treated with nitric acid. It does not undergo fermentation.

Salicin: $C_{13}H_{18}O_7$.—This glucoside occurs in the bark of many species of willow and poplar, also in the green parts of several spiræas, and in castoreum. It may also be prepared by the action of nascent hydrogen on helicin; or by treating populin with calcic or baric hydrate, when it is resolved into benzoic acid and salicin. Salicin crystallizes in broad colourless tables belonging to the trimetric system. It is insoluble in ether, but soluble in water and in alcohol; its solutions have a bitter taste. It melts at 120° (248° F.). A solution of salicin turns the plane of polarization to the left, the apparent specific rotatory power being $[\alpha]_r = -55^{\circ}\cdot 8$. As already noticed (p. 527), when treated with dilute acid, or submitted to the action of emulsin or synaptase, it is resolved into saligenol and glucose:

$$C_6H_4(CH_2.OH).O.C_6H_7O(OH)_4 \ + \ OH_2 \ = \ C_6H_4(OH).CH_2.OH \ + \ C_6H_{12}O_6.$$

When salicin is dissolved in an alcoholic solution of sodic ethylate, the liquid soon solidifies to a crystalline pulp of *sodium-salicin*, $C_{13}H_{17}NaO_7$ (Perkin, *Chem. News*, xviii. 110). At the ordinary temperature, acetic chloride converts salicin into a compound of acetic chloride with *tetracetylsalicin* of the composition $C_{13}H_{14}(C_2H_3O)_4O_7.C_2H_3OCl$. Tetracetylsalicin may be obtained from this, together with argentic chloride and acetic acid, by treatment with argentic nitrate. It crystallizes in needles, and is soluble in alcohol, ether, and water.

Chlorosalicin: $C_{13}H_{17}ClO_7,2OH_2$, is formed on passing chlorine into a mixture of one part of salicin with four of water until the crystals have dissolved. After a time, monochlorosalicin separates in slender silky needles. It is insoluble in ether, but soluble in water and in alcohol. By the continued action of chlorine, it is converted into *dichlorosalicin*, $C_{13}H_{16}Cl_2O_7,2OH_2$, which also crystallizes in long silky needles almost insoluble in ether and in cold water, but moderately soluble in alcohol. *Perchlorosalicin*, $C_{13}H_{15}Cl_3O_7,2OH_2$, is obtained as a yellow crystalline powder, by passing chlorine into hot water in which dichlorosalicin is suspended, and containing lumps of marble to neutralize the hydrochloric acid as it is formed. It is purified by washing it with ether, and subsequent crystallization from dilute alcohol. All these chlorine derivatives lose the two molecules of water of crystallization when heated to 100° (212° F.).

Bromosalicin: $C_{13}H_{17}BrO_7,2OH_2$, separates in a crystalline state on adding the requisite amount of bromine to salicin dissolved in 20 parts of water. It crystallizes from water in colourless four-sided prisms which lose their water of crystallization at 110° (230° F.) and fuse at 160° (320° F.). It is decomposed by emulsin with formation of *bromosaligenol*, $C_6H_3Br(OH).CH_2.OH$ (Schmidt, *Zeits. chem.*, i. 320).

Saponin, Struthin, Githagin, Senegin, Polygalin: $C_{32}H_{54}O_{18}$.—This glucoside, first discovered by Schrade in the common soapwort, *Saponaria officinalis*, has been obtained from the oriental soapwort, *Gysophila struthium*, from Quillaja bark, from the seeds of the corn cockle, *Agrostemma githago*, from senega root, from horse chestnuts, and the roots of numerous plants belonging to the natural orders *Polygalaceæ, Caryophyllaceæ* and *Primulaceæ*. It is obtained as a white amorphous fusible powder of peculiar aromatic odour, which is insoluble in ether and in dry alcohol, but soluble in dilute alcohol, and readily soluble in water, forming a liquid which froths on agitation. Its solution is precipitated by plumbic acetate. Dilute acids decompose saponin slowly in the cold, but more rapidly when heated, with formation of a glucose and separation of *sapogenin* (Rochleder, *Zeits. chem.*, iii. 632): $C_{32}H_{54}O_{18} + 2OH_2 = C_{14}H_{22}O_2 + 3C_6H_{12}O_6$. Sapogenin crystallizes in tufts of needles, which are soluble in alcohol and in ether.

The above equation only represents the final stage, however, there being two intermediate ones, the first resulting in the formation of a substance which

Fremy designated *æsculic acid:* $C_{32}H_{54}O_{18} = C_{26}H_{42}O_{12} + C_6H_{12}O_6$. In the second stage a gelatinous substance having the composition $C_{20}H_{32}O_7$ is produced: $C_{32}H_{54}O_{18} + OH_2 = C_{20}H_{32}O_7 + 2C_6H_{12}O_6$; whilst in some instances a compound, $C_{34}H_{54}O_9$, is obtained differing from sapogenin in being much more readily soluble in alcohol, and which may be regarded as derived from two molecules of sapogenin and one of a glucose, with elimination of water: $2C_{14}H_{22}O_2 + C_6H_{12}O_6 = C_{34}H_{54}O_9 + OH_2$.

Sinalbin: $C_{30}H_{44}N_2S_2O_{16}$ (?), a glucoside contained in mustard-seed, which, like potassic myronate, is decomposed by contact with an aqueous extract of mustard, yielding glucose, *acrinyl thiocyanate*, C_8H_7NSO, and *sinapisine sulphate*, $C_{16}H_{19}NSO_9$ together with an albuminous substance. Acrinyl thiocyanate is insoluble in water, soluble in ether, and resembles the allyl compound, but is not volatile (Will, *Zeits. chem.* [2], vii. 89).

Solanine.—An organic substance of basic nature discovered by Desfosses in the fruits of the *Solanum nigrum*, and since obtained from other plants belonging to the same genus, especially from the etiolated shoots and from the tubers of the potato. It is only slightly soluble in cold alcohol, but easily when it is hot, crystallizing out again on cooling in slender silky needles. It melts at 235° (455° F.), and is almost insoluble in water and in ether, but readily soluble in dilute acids, being precipitated again in a gelatinous state on the addition of an alkali. It is very poisonous. The composition of solanine is yet a matter of uncertainty, Zwenger and Kind (*Ann. Chem. Pharm.*, cix. 244; and cxviii. 129) assigning to it the formula, $C_{43}H_{71}NO_{16}$, whilst Kletzinsky (*Zeits. chem.* [2], ii. 127) makes it $C_{21}H_{35}NO_7$. Solanine forms both neutral and acid salts, which are mostly non-crystalline.

When solanine is boiled with dilute hydrochloric acid, it is decomposed with formation of a glucose and an alkaloïd, *solanidine*, to which Zwenger and Kind assign the formula, $C_{25}H_{41}NO$, representing the reaction which takes place in the following manner: $C_{43}H_{71}NO_{16} + 3OH_2 = C_{25}H_{41}NO + 3C_6H_{12}O_6$. The solanidine separates as hydrochloride, from which, after purification by crystallizing the salt from ether-alcohol, the base may be obtained by precipitating its alcoholic solution with ammonia. Solanidine is almost insoluble in water, but easily soluble in alcohol or ether, crystallizing in long colourless needles. Its solutions have a bitter, slightly astringent taste. The salts of solanidine, both neutral and acid, are only sparingly soluble in water or in dilute acids; most of them are crystalline.

A solution of solanidine in slightly diluted sulphuric, or cold concentrated hydrochloric acid, assumes a reddish or violet colour which passes into yellow, and on standing deposits a bulky yellow or brown precipitate. This consists of a mixture of the salts of two bases, one of which, in the free state, is soluble in ether, and appears to be impure solanidine, whilst the other, insoluble in ether, is *solanicine*, $C_{50}H_{73}N_2O$ (?). It is very slightly soluble in water and in alcohol, and requires 2000 parts of ether to dissolve it, crystallizing in slender needles on the spontaneous evaporation of the solution. Its salts are amorphous, and easily soluble in alcohol or water, but insoluble in ether.

It will readily be seen from this short notice that our knowledge of solanine and the products of its decomposition is very unsatisfactory; the whole subject requiring further investigation.

Syringin: $C_{19}H_{28}O_{10}.OH_2$.—This substance is obtained from the bark of the lilac, *Syringa vulgaris*, in which it occurs more abundantly in the month of March than in April. It is, according to Kromayer, identical with the *liqustrin* from privet bark. Syringin crystallizes from alcohol in long colourless needles which lose their water of crystallization at 115° (239° F.), and then melt at 212° (413°·6 F.). It is insoluble in ether, only sparingly soluble in cold, but readily in boiling water. When heated with dilute hydrochloric acid, syringin is decomposed, yielding a fermentable glucose and *syringenin:* $C_{19}H_{28}O_{10} + OH_2 = C_{13}H_{18}O_5 + C_6H_{12}O_6$. Syringenin, $C_{13}H_{16}O_4.OH_2$, is deposited in flocks which cohere to a pale rose-coloured amorphous mass. It loses a molecule of water at 100° (212° F.), and melts at 170°—180° (338°—356° F.). It is insoluble in water and in ether, but soluble in alcohol.

Tampicin: $C_{34}H_{54}O_{14}$.—A glucoside resembling convolvulin, found by Spirgatis (*N. Rep. Pharm.*, xix. 452) in Tampico jalap. It is a resinous substance, soluble in alcohol and in ether, which takes up $3OH_2$, and is converted into *tampicic acid*, $C_{34}H_{60}O_{17}$, when treated with a powerful base. On digesting tampicin with dilute acids, it is resolved into *tampicolic acid*, $C_{16}H_{32}O_3$, and glucose: $C_{34}H_{60}O_{17} + 4OH_2 = C_{16}H_{32}O_3 + 3C_6H_{12}O_6$. Tampicic acid is amorphous, and easily soluble in water and in alcohol. Tampicolic acid crystallizes in slender needles, and forms soluble salts with the alkalies; insoluble salts with the earths and heavy metals.

Tannins.—A number of substances occurring especially in the bark of plants and in the husks of fruit and seeds, which are mostly amorphous, of astringent taste, and precipitate albumen and gelatin from their solutions, and unite with animal membrane to form leather, are included under this designation. Two groups of tannins may be distinguished: those which are coloured black or bluish by ferric chloride, and those which are coloured green. Apparently the former yield a glucose and another substance when boiled with dilute acids, and pyrogallol on dry distillation; the latter, however, seldom furnish a glucose, but when submitted to the action of potassic hydrate frequently yield phloroglucol besides protocatechuic acid, and all furnish catechol (pyrocatechin) on dry distillation. Each group appears to contain a number of bodies differing in composition, but our knowledge of the majority of the tannins is extremely imperfect. *Gallotannin*, the chief constituent of the gallnuts of *Quercus infectoria* and of other species of oak, and of Chinese gallnuts, is a colourless amorphous substance, easily soluble in water, without action on polarized light. When boiled with dilute acids, it yields a dextroglucose and gallic acid, $C_6H_2(OH)_3.COOH$; from Schiff's experiments it is probable, however, that gallotannin is a glucoside of digallic acid, $C_{14}H_{10}O_9 = 2C_7H_6O_5 - OH_2$, most probably of the formula $C_{34}H_{28}O_{22}$, and that it yields a single molecule of glucose and two of digallic acid when decomposed, the latter being further resolved into gallic acid. Commercial tannin appears to be a mixture in variable proportions, according to the method of manufacture, of gallotannin (the glucoside) and of tannic or digallic acid, and sometimes to consist entirely of the latter, as when it yields no glucose on boiling with an acid.

Thujin: $C_{20}H_{22}O_{12}$.—A glucoside occurring in small quantity in the green parts of *Thuja occidentalis.* It crystallizes in minute, glistening, yellow plates, which are soluble in alcohol. When heated with dilute acids, it is decomposed into a glucose and *thujetin:* $2C_{20}H_{22}O_{12} + 4OH_2 = C_{28}H_{28}O_{16} + 2C_6H_{12}O_6$. Thujetin is almost insoluble in water, but soluble in alcohol and in ether. When boiled with baric hydrate solution it loses three molecules of water, and is converted into *thujetic acid*, $C_{28}H_{22}O_{13}$. This acid is also obtained by boiling thujin with baric hydrate solution in an atmosphere of hydrogen until a reddish-yellow precipitate is formed: $2C_{20}H_{22}O_{12} + OH_2 = C_{28}H_{22}O_{13} + 2C_6H_{12}O_6$. Thujetic acid crystallizes in lemon-yellow microscopic needles, soluble in alcohol, but insoluble in water.

When thujin is heated for a short time with hydrochloric acid only, *thujigenin*, $C_{28}H_{24}O_{14}$, appears to be formed. This compound may be obtained from the extract of *Thuja* by adding basic plumbic acetate to the filtrate, after the thujin, &c., has been removed by plumbic acetate. The precipitate is decomposed by hydric sulphide, and the clear solution evaporated in vacuo. Thujigenin forms microscopic needles soluble in alcohol, but only very slightly soluble in water.

Turpethin: $C_{34}H_{56}O_{16}$, a purgative resin extracted from the root of *Ipomœa turpethum*. It is easily soluble in alcohol, but, unlike jalapin, is insoluble in ether. It melts at 183° (361°·4 F.), and when boiled with dilute acids is resolved into glucose and *turpetholic acid:* $C_{34}H_{56}O_{16} + 6OH_2 = C_{16}H_{32}O_4 + 3C_6H_{12}O_6$. This acid may be obtained crystallized in colourless microscopic needles which melt at 88° (190°·4 F.). It is easily soluble in alcohol, less so in ether. The sodic salt, $C_{16}H_{31}NaO_4$, forms sharply-defined rhombic plates. Turpetholic acid is isomeric with jalapinolic acid, which is apparently homologous with convolvulinolic acid, the three acids being members of a series of the composition $C_nH_{2n}O_4$, to which glyceric acid belongs.

When turpethin is treated with baric hydrate solution, it takes up two molecules of water, and is converted into *turpethic acid*, $C_{34}H_{60}O_{18}$. It is an amorphous substance, easily soluble in water.

Xylosteïn or *Lonicerin*, a bitter glucoside said to exist in the berries of the fly honeysuckle, *Lonicera xylosteum*. The products of its decomposition have not yet been investigated.

From the foregoing description it will be evident that our knowledge of the glucosides is extremely imperfect: even their exact composition being unknown in many cases. In very few instances has it been ascertained that the glucose obtained from a particular glucoside is identical or not with sucrodextrose; and it is also at present doubtful whether those which furnish more than a single molecule of glucose are all glucosides, and not derived from a saccharon or even, as Hlasiwetz has suggested may be the case with some of the tannins, from a still higher carbohydrate of the nature of dextrin. A knowledge of the exact composition and constitution of the glucosides is now becoming of the greatest importance in connexion with the phenomena of vegetable life, and it is very desirable that they should receive a greater share of attention than has hitherto been devoted to them by chemists generally.

§ IV. The Thioethers and Polysulphides, Selenides, and Tellurides.

(1607) The thioethers are the analogues of the metallic sulphides, and bear the same relation to the ethers that the thioalcohols bear to the alcohols, thus:

Na_2S	$(C_2H_5)_2S$
Sodic sulphide.	Ethylic sulphide.

The following are known:

Thioethers of the $(C_nH_{2n+1})_2S$ *Series.*

		B. P. ° C.
Methylic sulphide	$CH_3.S.CH_3$	41°
Methylic ethylic sulphide	$CH_3.S.C_2H_5$	66°
Ethylic sulphide	$(C_2H_5)_2S$	91°
Propylic sulphide	$(C_3H_7)_2{}^\alpha S$	130°–135°
Isopropylic sulphide	$(C_3H_7)_2{}^\beta S$	116°–120°
Ethylic isoamylic sulphide	$C_2H_5.S.C_5H_{11}$	158°
Butylic sulphide	$(C_4H_9)_2{}^\alpha S$	182°
Isoprimary butylic sulphide	$(C_4H_9)_2{}^\beta S$	173°
Secondary butylic sulphide	$(C_4H_9)_2{}^\gamma S$	165°
Isoamylic sulphide	$(C_5H_{11})_2S$	216°

Thioethers derived from other Monothioalcohols.

		B. P. °C.
Allylic sulphide	$(C_3H_5)_2S$	140°
Phenylic sulphide	$(C_6H_5)_2S$	293°
Benzylic sulphide	$(C_6H_5.CH_2)_2S$	M.P. 49°
α-Naphthylic sulphide	$(C_{10}H_7)_2{}^{\alpha}S$	M.P. about 100°

Preparation.—Thioethers may be prepared by the following methods, all of which are of more or less general application.

1. By the action of haloid derivatives of hydrocarbons, or of the salts formed by neutralizing the acid ethereal sulphates with an alkali or alkaline-earthy carbonate, on potassic or sodic sulphide; for example (comp. footnote, p. 707):

$$\underset{\text{Ethylic chloride.}}{2C_2H_5Cl} + K_2S = \underset{\text{Ethylic sulphide.}}{(C_2H_5)_2S} + 2KCl.$$

$$\underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} + K_2S = \underset{\text{Ethylenic sulphide.}}{C_2H_4S} + 2KBr.$$

$$\underset{\text{Potassic ethylic sulphate.}}{2C_2H_5.KSO_4} + K_2S = \underset{\text{Ethylic sulphate.}}{(C_2H_5)_2S} + 2K_2SO_4.$$

The usual plan is to digest a mixture of the haloid hydrocarbon derivative with a concentrated aqueous or alcoholic solution of the sulphide; or if the sulphate be employed, to distil it with a concentrated solution of the sulphide. It need scarcely be stated that only certain of the haloid derivatives of hydrocarbons are available for the preparation of corresponding sulphides, those derived from hydrocarbons in which the carbon atoms are regarded as entirely or partially united in a closed chain by the displacement of hydrogen atoms attached to carbon atoms which form part of the closed chain being without action on the metallic sulphides, whereas those in which the halogen is contained in the side chain, as a rule, readily furnish corresponding sulphides. Thus the modification of monochlorotoluene termed benzylic chloride, $C_6H_5.CH_2Cl$, at once reacts with potassic and sodic sulphide, whereas the chlorotoluenes of the formula $C_6H_4Cl.CH_3$ are not in the least affected by these reagents. Isomeric haloid derivatives of hydrocarbons in which the carbon atoms may be regarded as forming an open chain may also act very differently; thus of the two dibromethanes $CH_2Br.CH_2Br$ and $CH_3.CHBr_2$, only the former is converted into the corresponding sulphide by the action of potassic or sodic sulphide.

2. The previous method is available only for the preparation of simple thioethers, but by the action of the haloid derivatives of hydrocarbons on the potassium and sodium and other metallic derivatives of the thioalcohols both mixed and simple thioethers may be obtained; thus:

$$\underset{\text{Sodic ethylic sulphide.}}{C_2H_5.SNa} + CH_3I = \underset{\text{Methylic ethylic sulphide.}}{C_2H_5.S.CH_3} + NaI.$$

$$\underset{\text{Sodic ethylic sulphide.}}{2C_2H_5.SNa} + \underset{\text{Methylenic iodide.}}{CH_2I_2} = \underset{\text{Methylenic ethylic sulphide.}}{CH_2(S.C_2H_5)_2} + 2NaI.$$

$$\underset{\text{Sodic ethylic sulphide.}}{3C_2H_5.SNa} + \underset{\text{Chloroform.}}{CHCl_3} = \underset{\text{Thioethylic orthoformate.}}{CH(S.C_2H_5)_3} + 3NaCl.$$

$$\underset{\text{Sodic ethylic sulphide.}}{4C_2H_5.SNa} + \underset{\substack{\text{Tetrachloro-}\\\text{methane.}}}{CCl_4} = \underset{\substack{\text{Thioethylic ortho-}\\\text{carbonate.}}}{C(S.C_2H_5)_4} + 4NaCl.$$

The remarks above made with regard to the kind of haloid derivatives available for the preparation of thioethers are equally applicable in the present case. The formation of thioethers, in this manner is far more easily effected than that of the ethers by the corresponding reactions; it appears, moreover, that in the formation of the thioethylic ethers the reaction takes place the less readily between the sodic thioethylate and the haloid derivative the greater the number of carbon atoms in the latter: much more heat being developed, and the reaction taking place much more readily, when methylic or ethylic iodide, for example, acts upon sodic thioethylate, than when amylic chloride is employed; similarly, tetrachloromethane is more readily converted into the thioether than hexachlorethane, and tetrachlorethylene is far less active than either of the former. (Claesson, *Jour. pr. Chem.* [2], xv. 212.)

3. A third method, which is available for the preparation of thioethers corresponding to the thiophenols, as well as of those corresponding to the thiocarbinols, consists in submitting the plumbic and other metallic derivatives of the thioalcohols to dry distillation:

$$\underset{\text{Plumbic thiophenate.}}{(C_6H_5.S)_2Pb} = PbS + \underset{\text{Phenylic sulphide.}}{(C_6H_5)_2S.}$$

Properties.—The thioethers are mostly colourless or yellow liquid bodies, insoluble or nearly so in water, but soluble in alcohol, ether, &c. It is usually stated that they possess highly offensive odours, but this, in most cases, is probably true only of the impure substances.

On oxidation with nitric acid they are converted into compounds such as $(C_2H_5)_2SO$, $(C_2H_5)SO_2$, $(C_6H_5)_2SO_2$, the thioethers derived from the thiocarbinols yielding both monoxides (*sulphines*) and dioxides (*sulphones*), whilst those derived from the thiophenols apparently furnish only compounds of the latter class.

The thioethers derived from the thiocarbinols are also characterized by the property of uniting directly with the moniodoparaffins to form crystalline compounds such as $(C_2H_5)_3SI = (C_2H_5)_2S + C_2H_5I$. These compounds are converted into corresponding hydroxides or hydrates by the action of argentic hydroxide or hydrate: $(C_2H_5)_3S.I + AgOH = AgI + (C_2H_5)_3S.OH$; the bodies so produced being in every respect analogous to the metallic hydroxides such as potassic hydroxide. They are very soluble in water, and furnish caustic, strongly alkaline solutions, which absorb carbonic anhydride on exposure to the air; they neutralize acids,* forming corresponding salts: $(C_2H_5)_3S.OH + HNO_3 = (C_2H_5)_3S.NO_3 + OH_2$; they precipitate metallic hydroxides from solutions of metallic salts: $2(C_2H_5)_3S.OH + ZnSO_4 = Zn(OH)_2 + [(C_2H_5)_3S]_2SO_4$; and they furnish crystalline chloroplatinates: $H_2PtCl_6 + 2(C_2H_5)_3S.OH = [(C_2H_5)_3S]_2PtCl_6 + 2OH_2$.

Several compounds of the thioethers derived from the thiocarbinols with metallic salts, such as $(C_2H_5)_2S.HgCl_2$, have also been obtained.

(1608) ETHYLIC SULPHIDE or *Thioethylic Ether:* $(C_2H_5)_2S$.—This compound is most conveniently prepared by passing ethylic chloride prepared by Groves' method (1176) into an alcoholic solution of potassic sulphide, which is gently heated in a flask or retort attached to a reversed condenser; after a time the product is distilled off, well washed with water, dried over calcic chloride and rectified. The solution of sulphide is prepared by saturating one-half of a con-

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* Thomsen (*Jour. pr. Chem.* [2], xiii. 241) has shown that on neutralizing aqueous solutions of the hydroxides by hydrochloric and sulphuric acids almost as much heat is developed by the hydroxide $(C_2H_5)_3S.OH$ as by those of the alkali and alkaline-earthy metals; thus:

	$2HCl.$	$H_2SO_4.$
$2Li.OH$	27,700 heat units	31,290 heat units.
$2Na.OH$	27,490 „	31,380 „
$2K.OH$	27,500 „	31,290 „
$2Tl.OH$	27,520 „	31,130 „
$Ba(OH)_2$	27,780 „	—— „
$Sr(OH)_2$	27,630 „	30,710 „
$Ca(OH)_2$	27,900 „	31,140 „
$2(C_2H_5)_3S.OH$	27,440 „	30,700 „

centrated alcoholic solution of potassic hydrate with sulphuretted hydrogen, and then mixing it with the other half. Ethylic sulphide may also be prepared by the aid of ethylic bromide or iodide, or of potassic or sodic ethylic sulphate; it is formed on adding sodic thioethylate to a solution of potassic ethylic sulphate, warming gently for a short time, and then distilling; and when a solution of potassic hydrate and potassic ethylic sulphate is mixed with thioethylic alcohol and the mixture distilled: this latter method can be employed with advantage for the preparation of ethylic sulphide perfectly free from thioethylic alcohol (Claesson).*

The crude thioethylic alcohol prepared by distilling a solution of potassic thiohydrate with potassic or sodic ethylic sulphate invariably contains ethylic sulphide; when the potassic salt is employed, the reaction takes place more rapidly and at a lower temperature, and relatively much less sulphide (about 10 per cent.) is produced, than when the sodic salt is used, the latter furnishing about 20 per cent. of sulphide. If during the distillation, however, the solution be kept saturated with sulphuretted hydrogen, the oil which passes over contains only about 4 per cent. of sulphide. The explanation of this appears to be that when a solution of potassic thiohydrate is heated, sulphuretted hydrogen is given off, potassic hydrate being produced, and thus the conditions necessary to the formation of the sulphide are realized; but by passing in sulphuretted hydrogen, the formation of potassic hydrate is in great measure prevented, and hence very little sulphide is formed (Claesson).

Ethylic sulphide is a colourless, mobile, inflammable liquid, of most unpleasant alliaceous odour (?), insoluble in water, but readily soluble in alcohol and ether; it boils at 91° (195°·8 F.), and at 20° (68° F.) has the sp. gr. ·825. It combines with mercuric chloride, forming the compound $(C_2H_5)_2S.HgCl_2$, which crystallizes in monoclinic prisms; platinic chloride also unites with it, forming the compound $2(C_2H_5)_2S.PtCl_4$. It is violently acted upon by chlorine, yielding a series of substitution derivatives which have not yet been sufficiently examined, however. When acted upon by nitric acid of sp. gr. 1·2, it is converted into the monoxide $(C_2H_5)_2SO$, whereas the fuming acid converts it into the dioxide or diethylsulphone, $(C_2H_5)_2SO_2$. According to R. H. Smith (*Jour. Chem. Soc.*, xxii. 302), it is converted, on treatment with concentrated sulphuric acid, into an acid of the composition $C_2H_6S_2O_3$, which yields crystalline salts, such as the baric salt $(C_2H_5)_2S_4O_6Ba$; the nature of this acid has not been ascertained, but it appears probable that it is the analogue of hydric ethylic sulphate

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* From the manner in which the heat is developed on mixing dilute aqueous solutions of potassic hydrate and of sulphuretted hydrogen, it appears that only the reaction represented by the equation $KOH + H_2S = KSH + OH_2$ takes place, and that the sulphide K_2S is not produced even when a considerable excess of potassic hydrate is employed (Thomsen); from this there can be little doubt that the sulphides K_2S and Na_2S are decomposed when dissolved in water with formation of sulphydrate and hydrate, the decomposition being more or less complete according to the amount of water present. But if this be the case, the formation of ethylic sulphide is at most only partially due to the reaction $K_2S + 2C_2H_5Cl = 2KCl + (C_2H_5)_2S$; probably the greater part of the sulphide is produced, as Claesson has suggested (*Jour. pr. Chem.* [2], xv. 218), by the successive occurrence of the following reactions:

$$\begin{aligned} KSH &+ C_2H_5Cl = C_2H_5.SH + KCl. \\ C_2H_5.SH &+ KOH = C_2H_5.SK + OH_2. \\ C_2H_5.SK &+ C_2H_5Cl = (C_2H_5)_2S + KCl. \end{aligned}$$

produced by the action of the acid on the thioethylic alcohol present as impurity in the sulphide employed: $C_2H_5.SH + H_2SO_4 = C_2H_5S.SO_2.OH + OH_2$. An aqueous solution of potassic hydrate is without action on ethylic sulphide, but when it is distilled over the solid hydrate, it is partially decomposed with formation of alcohol and potassic sulphide. On gently warming a mixture of ethylic sulphide and ethylic iodide, the two substances unite to form a crystalline compound of the formula $(C_2H_5)_3SI$; this compound and its homologues are described in section 1612.

(1609) *Higher Sulphides of Ethyl—Ethylic Disulphide:* $(C_2H_5)_2S_2$.—This compound is most readily obtained in the pure state by the action of iodine on the thioethylates: $2C_2H_5.SNa + I_2 = 2NaI + (C_2H_5)_2S_2$. It is also formed on heating thioethylic alcohol with sulphur for about six hours at 150° (302° F.): $2C_2H_5.SH + S = (C_2H_5)_2S_2 + SH_2$; and together with higher sulphides by distilling 'liver of sulphur' with a solution of potassic or sodic ethylic sulphate. It is a colourless oil, of about the sp. gr. of water, possessing a most unpleasant odour; it boils at 151° (303°·8 F.). Like the monosulphide, it produces a precipitate in an alcoholic solution of mercuric chloride, and in solutions of several other metallic salts. When oxidized by nitric acid, it is converted into the oxide $(C_2H_5)_2S_2O_2$, which on further oxidation yields ethylsulphonic acid, $C_2H_5.SO_3H$. Bodies which apparently are chlorinated derivatives of ethylic bisulphide have been obtained by Guthrie by the action of the chlorides of sulphur on ethylene.

Ethylic sulphide is not in the least affected by heating with sulphur, and it may therefore be freed from thioethylic alcohol by this means, but when the disulphide is heated with sulphur at 150° (302° F.), it is converted into the trisulphide (Müller, *Jour. pr. Chem.* [2], iv. 34), $(C_2H_5)_2S_3$. This compound cannot be distilled except in a current of steam; it is a heavy yellow oil, which may be deprived of the third atom of sulphur without difficulty, being slowly converted into the disulphide by shaking with metallic mercury or with potassic hydrate solution; it is not altered, however, by heating with thioethylic alcohol at 150° (302° F.). On oxidation with nitric acid, it yields ethylsulphonic and sulphuric acids.

Ethylic Tetrasulphide: $(C_2H_5)_2S_4$, is obtained when a solution of sulphur chloride, S_2Cl_2, in carbonic bisulphide is added to a similar solution of sodic thioethylate (Claesson, *ibid.* [2], xv. 214). It is a heavy yellow oil, possessing an extremely unpleasant, persistent odour, easily soluble in ether, but with difficulty in alcohol. It is decomposed into the bisulphide and sulphur on distillation alone, but when distilled with vapour of water, it is in great part split up into sulphur and ethylic trisulphide. On oxidation with nitric acid, it yields sulphur and ethylsulphonic acid. It dissolves a considerable quantity of sulphur at 150° (302° F.), and perhaps combines with it to form a pentasulphide.

(1610) *Homologues of Ethylic Sulphide.*—These compounds are obtained by methods precisely similar to those employed in the preparation of ethylic sulphide, and they exhibit the closest resemblance to this latter compound in their properties generally. The first term of the series, methylic sulphide, $(CH_3)_2S$, enters into reaction with other substances far more readily than the homologous compounds. It combines directly with bromine to form a crystalline bromide, $(CH_3)_2SBr_2$, the reaction being attended with the development of much heat; this bromide is converted into the corresponding oxide, $(CH_3)_2SO$, on treatment with moist argentic oxide. It also forms a crystalline compound with hydriodic acid when it is saturated with the gas at a low temperature; the product is decomposed, however, into its generators when mixed with water, and when heated in closed tubes, it yields thiomethylic alcohol and the compound $(CH_3)_3SI$. Comparatively little is known of the remaining thioethers of the $(C_nH_{2n+1})_2S$ series, their behaviour on oxidation having been chiefly studied (comp. Saytzeff, *Ann. Chem. Pharm.*, cxxxix. 354; cxliv. 148; Claesson, *Jour. pr. Chem.* [2], xv. 174).

(1611) *Compounds formed by the Union of the Thioethers of the* $(C_nH_{2n+1})_2S$ *Series with the Moniodoparaffins.*—The formation of these compounds is expressed by the general equation

$$(C_nH_{2n+1})_2S \ + \ C_nH_{2n+1}I \ = \ S(C_nH_{2n+1})_3I.$$

Apparently, this reaction takes place the more readily the fewer the number of carbon atoms contained both in the thioether and in the iodide; thus methylic sulphide and methylic iodide at once enter into reaction at the ordinary temperature and a considerable amount of heat is developed by their union, but ethylic sulphide and ethylic iodide only slowly combine, so that in preparing the triethiodide, $S(C_2H_5)_3I$, it is desirable to heat the mixture to about 100° (212° F.). It is not requisite that both the thioether and iodide should contain the same radicle, although there is apparently a greater tendency to form the compounds containing only similar radicles, a mixture of methylic sulphide and ethylic iodide yielding, for example, a mixture of the trimethiodide, $S(CH_3)_3I$, and triethiodide, $S(C_2H_5)_3I$ (Dehn). Similarly, when benzylic sulphide is submitted to the action of methylic iodide, a mixture of the trimethiodide $S(CH_3)_3I$ and of the benzyldimethiodide $S(C_7H_7)(CH_3)_2I$ is produced, the formation of which may be accounted for in the following manner:—

$$2CH_3I \ + \ (C_7H_7)_2S \ = \ (CH_3)_2S \ + \ 2C_7H_7I.$$

$$(CH_3)_2S \ + \ C_7H_7I \ = \ S(C_7H_7)(CH_3)_2I. \quad (CH_3)_2S \ + \ CH_3I \ = \ S(CH_3)_3I.$$

Probably, however, in all these cases the iodide and sulphide unite directly in the first instance, and the compounds with similar radicles are formed by the subsequent decomposition of the resulting 'mixed' derivative.

The thioethers also unite with the monobromoparaffins, but far less readily than with the moniodoparaffins, and as only traces of the triethylchloride $S(C_2H_5)_3Cl$ are formed by prolonged heating of a mixture of ethylic sulphide and chloride at 100° (212° F.), there can be little doubt that the chloroparaffins will be found to exhibit still less tendency to combine with the thioethers.

Hitherto no attempt has been made to prepare compounds containing three dissimilar hydrocarbon radicles, and only the methyl and ethyl compounds have been investigated: they have been studied by Oefele, to whom we owe the discovery of this property of the thioethers, *Ann. Chem. Pharm.*, cxxxii. 82; Dehn, *ibid.*, *Sup.* iv. 83; Cahours, *ibid.*, cxxxv. 352; cxxxvi. 151; *Compt. Rend.*, lxxx. 1317; Schöller, *Deut. chem. Ges. Ber.*, vii. 1274; and Krüger, *Journ. pr. Chem.* [2], xiv. 193.

Sulphur Triethiodide: *$S(C_2H_5)_3I$, is best prepared by heating a mixture of ethylic iodide and sulphide in molecular proportions for about an hour at 105°—110° (221°—230° F.); the mixture remains perfectly colourless, and after about fourteen days at least half is deposited in the form of brilliant white crystals of the iodide (Dehn). It is also formed on heating thioethylic alcohol with ethylic iodide at 140° (284° F.) for 6—7 hours (Dehn), or with hydriodic acid (Cahours); thioethylic alcohol cooled in a refrigerating mixture of ice and salt readily absorbs dry hydriodic acid gas, but without forming a crystalline compound: on heating the saturated solution for twenty-four hours at 100° (212° F.), sulphuretted hydrogen and sulphur triethiodide are produced.

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* Oefele regarded the group $S(C_2H_5)_3$ as analogous in composition with triethylamine, $N(C_2H_5)_3$, and therefore named this compound *triethysulphine iodide*, and the term sulphine has since been applied to all the compounds of similar constitution. But the analogy is obviously incomplete as triethylamine combines directly with acids, which is not the case with 'triethylsulphine,' which moreover cannot be isolated. It appears desirable, therefore, to apply names to these compounds similar to those employed for the organo-metallic compounds.

It crystallizes in rhombic prisms, and is very soluble in water and in warm, strong alcohol, but only with difficulty soluble in ether; it melts a little above 100° (212° F.), being entirely decomposed into its generators. The chloride $S(C_2H_5)_3Cl$, which may be obtained by agitating a solution of the iodide with freshly precipitated argentic chloride, crystallizes in long white glistening needles. It forms with mercuric chloride a double chloride, $S(C_2H_5)_3Cl, 4HgCl_2$, which crystallizes in glistening needles or plates. The platinochloride, $Pt[S(C_2H_5)_3]_2Cl_6$, crystallizes on slow evaporation of a moderately concentrated solution in magnificent garnet-red monoclinic prisms. The hydroxide, $S(C_2H_5)_3.OH$, which is obtained by treating a solution of the chloride, bromide, or iodide with a slight excess of argentic hydroxide and evaporating in vacuo, forms deliquescent crystals which attack the skin like potassic hydrate; it expels ammonia from its salts on warming, and precipitates the solutions of various metallic salts; by neutralizing it with various acids, salts such as the nitrate, $S(C_2H_5)_3.NO_3$, and sulphate $[S(C_2H_5)_3]_2SO_4$, are produced, and may be obtained in crystals by carefully concentrating the solutions.

Sulphur Trimethiodide: $S(CH_3)_3I$, and the various compounds formed from it by displacing the iodine by other negative radicles, exhibit the closest resemblance to the corresponding triethyl compounds.

Sulphur Diethmethiodide: $S(C_2H_5)_2(CH_3)I$.—This compound may be obtained by combining ethylic sulphide with methylic iodide, or methylic ethylic sulphide with ethylic iodide, the combination being effected by heating the mixture of thioether and iodide to which a little water has been added on the water bath in a flask attached to a reversed condenser until the whole forms a homogeneous reddish-brown liquid. Unless water is added, the combination does not appear to take place under the ordinary pressure; and if a mixture of ethylic sulphide and iodide in molecular proportions is heated in a sealed tube at 120° (248° F.) for several days, a mixture of sulphur trimethiodide and triethiodide is obtained. According to Krüger, however, the two products obtained from ethylic and methylic ethylic sulphide respectively are not identical, but isomeric: *Sulphur diethmethiodide*, as the compound formed from ethylic sulphide and methylic iodide may be termed, and all the simple salts formed from it by displacing the iodine by negative radicles, being so extremely soluble and deliquescent as to be uncrystallizable, whereas the *ethmethethiodide* crystallizes in long extremely deliquescent needles, and furnishes a series of double salts which are throughout deeper in colour than those of the same composition derived from the diethmethiodide and also crystallize differently and exhibit lower melting points, as will be evident from the following descriptions; moreover, the diethmethylchloride combines with *six* molecules of mercuric chloride, whereas the ethmethethylchloride combines with only *two* molecules of this salt:*

Diethylmethyl Compounds.

Platinochloride: $[S(C_2H_5)_2(CH_3)]_2PtCl_6$, crystallizes in forms of the regular system, and melts at 214° (417°·2 F.); the crystals, which are of a light-red colour, are reduced to a yellow powder when dried over calcic chloride.

Aurichloride: $[S(C_2H_5)_2(CH_3)]AuCl_4$.—Long pale-yellow needles, melting at 192° (377°·6 F.).

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* From this it would appear that the several 'units of affinity' of sulphur are not of the same value. The discussion of this question may, however, conveniently be postponed for consideration later on (see hydroxamines).

Hydrargyrochloride: $S(C_2H_5)_2(CH_3)Cl.6HgCl_2$.—Hexagonal plates, which melt at 190°(388°·4 F.).

Hydrargyrocyaniodide: $S(C_2H_5)_2(CH_3)HgCNI_2$.—Pale-yellow tetragonal crystals, which melt at 115° (239° F.).

Ethylmethylethyl Compounds.

Platinochloride: $[S(C_2H_5)_2(CH_3)]_2PtCl_6$.—Dark-red monoclinic prisms, which become rose-red on drying, and then melt at 186° (366°·8 F.); by long continued digestion of its aqueous solution it may be converted into the isomeride of higher melting point, but the reverse change has not been effected.

Aurichloride: $[S(C_2H_5)_2(CH_3)]AuCl_4$.—Always separates from solution as a sulphur-yellow microcrystalline powder, and melts at 178° (252°.4 F.).

Hydrargyrochloride: $S(C_2H_5)_2(CH_3)Cl.2HgCl_2$.—Rhombic plates, melting at 112° (233°·6 F.).

Hydrargyrocyaniodide: $S(C_2H_5)_2(CH_3)HgCNI_2$.—Amber-yellow monoclinic prisms, which melt at 98° (208°·4 F.).

It is a curious fact that mercuric sulphide always separates as the black modification on decomposing the hydrargyrochlorides by sulphuretted hydrogen, whereas the double salts formed with the aid of mercuric cyanide furnish the red sulphide.

(1612) *Compounds formed by the Union of the Thioethers with Dihaloid Paraffin Derivatives.*—According to Dehn, when a mixture of ethylic sulphide and ethylenic bromide in molecular proportions with one-half to its own volume of water is heated in sealed tubes at 125°—130° (257°—266° F.), ethylic bromide and diethylenic disulphide are produced, together with sulphur triethylbromide, and a compound which he represents by the formula $S(C_2H_4)(C_2H_5)_2Br_2$, but which is more probably a compound of the formula $S(C_2H_4Br)(C_2H_5)_2Br$; a resinous product is also formed, and the aqueous solution appears to contain other substances besides those mentioned. Cahours states that by heating a mixture of 1 vol. ethylenic bromide and 2 vols. methylic sulphide at 100° (212° F.), a crystalline compound is gradually formed, having the formula $C_6H_{16}Br_2S_2 =$ (?) $C_2H_4[S(CH_3)_2Br]_2$; and that monobromethylenic bromide yields the compound $C_8H_{21}Br_3S_3 =$ (?) $C_2H_3[S(CH_3)_2Br]_3$.

(1613) ALLYLIC SULPHIDE: $(C_3H_5)_2S$.—This compound is the chief constituent of the oils of garlic and onion, although apparently it is not usually present as such in the plants, but is formed during the distillation from some more complex substance; it is also obtained mixed with the thiocyanate from a number of plants which yield sulphur-containing oils, such as *Thlaspi arvense*, *Erysimum aliaria*, &c. It may be prepared artificially by the action of allylic bromide or iodide on a solution of potassic sulphide.

Allylic sulphide is a colourless oil, of sharp, unpleasant odour, lighter than water, in which it is only slightly soluble; it boils at 140° (284° F.). It combines with argentic nitrate when mixed with an alcoholic solution of this salt; a precipitate being obtained which when re-crystallized from hot water forms white needles of the composition $(C_3H_5)_2S.2AgNO_3$. It also yields precipitates with other metallic salts, but the compounds produced have been very insufficiently examined. It appears to combine with the iodoparaffins, and on carefully mixing it with bromine in presence of ether, colourless needles, probably of the composition $(C_3H_5Br_2)_2S$, are obtained.

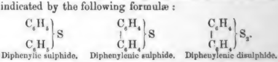
(1614) PHENYLIC SULPHIDES.—Phenylic sulphide, $(C_6H_5)_2S$, may be obtained by the destructive distillation of the metallic derivatives of thiophenol, or of sodic benzenesulphonate, $C_6H_5.SO_3Na$ (Stenhouse, *R. Soc. Proc.* xiv. 353; xvii. 62), and by the decomposition by heat of the thiophosphates formed by the action of the sulphides of phosphorus on phenol (Kekulé).

It is a nearly colourless oil of aromatic, slightly alliaceous odour, insolu water, but very soluble in hot alcohol, ether, benzene, and carbonic bisulp it boils at 292° (557°·6 F.). Its alcoholic solution is not precipitated by arg nitrate or mercuric chloride; it is also incapable of combining with the paraffins. When oxidized by concentrated nitric acid or chromic acid mixtu is converted into diphenylsulphone or sulphobenzid, $(C_6H_5)_2SO_2$. It is dissolv warm concentrated sulphuric acid, being apparently converted into an acid formula $C_6H_6S_2O_3$ (Stenhouse).

Phenylic Disulphide: $(C_6H_5)_2S_2$, which may be prepared from thiophen a variety of ways (1580), crystallizes in long white shining needles or developed prisms, which melt at 60° (140° F.); by the action of na hydrogen it is converted into thiophenol, and on oxidation yields benzenesulp acid. It combines with bromine forming the compound $(C_6H_5)_2S_2Br_2$, crystallizes in nacreous laminæ. No higher sulphides of phenyl are known

(1615) PHENYLENIC SULPHIDES.—On passing phenylic sulphide thr a red-hot tube, it is converted by the withdrawal of two atoms of hydrogen *diphenylenic sulphide*, $C_{12}H_8S$ (Stenhouse, *op. cit.*, xviii. 542; Græbe, *chem. Ges. Ber.*, vii. 50). This compound crystallizes from alcohol in needles, which melt at 94° (201·2 F.; Stenhouse) (97° or 206°·6 F.; Gr on oxidation, it is converted into *diphenylenesulphone*, $C_{12}H_8SO_2$.

Diphenylenic Disulphide: $C_{12}H_8S_2$, which is also a product of the de position by heat of sodic benzenesulphonate and of the thiophosphates forme treating phenol with phosphoric pentasulphide (Stenhouse, Græbe), crysta in long lustrous prisms, which melt at 159° (318°·2 F.; S.) (153° or 30 F.; G.); it dissolves in warm concentrated sulphuric acid, forming a soluti a magnificent purple colour, from which water precipitates the apparently altered sulphide. The relation of the two phenylene sulphides to phenylic sulp is probably indicated by the following formulæ:



$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}S \qquad \left.\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\right\}S \qquad \left.\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\right\}S_2.$$

Diphenylic sulphide. Diphenylenic sulphide. Diphenylenic disulphide.

(1616) BENZYLIC SULPHIDE: $(C_6H_5.CH_2)_2S$. This compound is prep by the action of benzylic chloride on an alcoholic solution of potassic sulph It crystallizes in white needles, which melt at 49° (120°·2 F.); on distilla it is decomposed with formation of sulphuretted hydrogen, toluene, stilbene, other products. Nitric acid of sp. gr. 1·3 converts it into the oxide (C_7H_7) which on further oxidation yields benzoic acid. Its behaviour on heating methylic iodide has already been described.

(1617) ETHYLENIC SULPHIDE: C_2H_4S.—By the action of *a*-dibromethan ethylenic bromide on an alcoholic solution of potassic sulphide, a white amorph substance of the composition C_2H_4S is produced; on heating this subst either alone or with carbonic bisulphide in sealed tubes at 160°—170° (320 338° F.) for several days, it is converted into a crystalline body of the empirical composition but having a vapour density corresponding to the for $(C_2H_4)_2S_2$ (Husemann, *Ann. Chem. Pharm.*, cxxvi. 280). The substance is produced on heating ethylenic thiocarbonate, or the mer derivative of thioglycol, with ethylenic bromide at 150° (302° F.). Diethy disulphide readily dissolves in hot alcohol, ether, and carbonic bisulp crystallizing from alcohol in needles and laminæ, and from ether in monoclinic prisms; it melts at 112° (233°·6 F.), and boils at about 200° (392 Its alcoholic solution yields crystalline precipitates with auric, mercuric, platinic chlorides, and with argentic nitrate; and by adding bromine t solution in carbonic bisulphide, the compound $(C_2H_4)_2S_2Br_4$ is obtained lemon-yellow amorphous precipitate which is decomposed by water into hydrobromic acid and the oxysulphide $(C_2H_4)_2S_2O_2$. Corresponding compounds may be formed containing chlorine or iodine. The same oxysulphide is produced on oxidizing the sulphide with nitric acid.

On treatment with potassic sulphide methylenic iodide and propylenic bromide are also converted into amorphous sulphides, which like the ethylenic compound is nearly insoluble in all neutral solvents; the methylenic compound is converted into a crystalline modification at about 150° (302° F.), but the propylenic sulphide is decomposed when heated (Husemann).

(1618) SELENIUM ETHERS—*Methylic Selenide:* $(CH_3)_2S$.—To prepare this compound, phosphoric pentaselenide is added to a concentrated solution of sodic hydrate and potassic methylic sulphate, and the mixture distilled; by the action of the sodic hydrate on the pentaselenide, sodic selenide is produced, which then acts upon the potassic methylic sulphate. The product is purified by fractional distillation. It is a colourless, highly refractive, inflammable liquid, of extremely unpleasant odour (due probably to the diselenide), boiling at 58° (136°·4 F.); it is not miscible with water, but dissolves readily in alcohol and ether. If it be dissolved in nitric acid, and the solution be then evaporated on the water-bath, a crystalline residue of the nitrate (?) $(CH_3)_2Se(OH).NO_3$ is obtained; on adding the haloid acids to solutions of the nitrate, crystalline precipitates of the chloride, $(CH_3)_2SeCl_2$, and of the corresponding bromide and iodide are produced (Jackson, *Ann. Chem. Pharm.*, clxxix. 1).

Ethylic Selenide: $(C_2H_5)_2Se$.—This compound is produced together with the diselenide by the method above described, substituting potassic ethylic sulphate in place of potassic methylic sulphate; the two substances are separated by fractional distillation (Rathke, *ibid.*, clii. 210). It is a colourless liquid, resembling ethylic sulphide in odour, the intensely unpleasant smell usually ascribed to it being due to the diselenide; it boils at 108° (226°·4 F.). The diselenide, $(C_2H_5)_2Se_2$, is a yellow liquid, and boils at 186° (366°·8 F.). Ethylic selenide dissolves in nitric acid, forming the nitrate $(C_2H_5)_2Se(NO_3)_2$, from which the corresponding chloride, bromide, and iodide may be obtained by the addition of the haloid acids to the solution. According to Rathke, it is not possible to prepare a selenium tetrethide from the dichloride by the action of zincic ethide, the reaction taking place in accordance with the equation:

$$2(C_2H_5)_2SeCl_2 \; + \; Zn(C_2H_5)_2 \; = \; 2Se(C_2H_5)_3Cl.ZnCl_2.$$

According to Cahours, methylic and ethylic selenides combine directly with the iodoparaffins, forming compounds analogous to those obtained in a similar manner from the thioethers.

Whereas sulphur is finally oxidized to sulphuric acid by the action of nitric acid, selenium under similar conditions is converted only into selenious acid; in like manner, methylic and ethylic diselenides furnish the selenious compounds $CH_3.SeO_2H$ and $C_2H_5.SeO_2H$ on oxidation with nitric acid. These acids form crystalline compounds with hydrochloric acid, such as $CH_3.SeO_2H.HCl =$? $CH_3.Se(OH)_2Cl$, which may be obtained by dissolving the selenides in nitric acid, and then adding hydrochloric acid; these compounds are reduced by sulphurous acid, furnishing the pure diselenide.

Benzylic Selenide: $(C_6H_5.CH_2)_2Se$, prepared in the same manner as the methyl compound, crystallizes in long white needles or monoclinic prisms, which melt at 45°·5 (113°·9 F.). It furnishes a crystalline nitrate and chloride, and an amorphous platinochloride, $[(C_7H_7)_2Se]_2PtCl_4$; these compounds are all extremely unstable, however, and decompose in the manner represented by the equation $(C_7H_7)_2SeCl_2 = 2C_7H_7Cl + Se$, and not, as the ethyl and methyl compounds, into their generators: $(CH_3)_2SeBr_2 = (CH_3)_2Se + Br_2$.

Benzylic Diselenide: $(C_7H_7)_2Se_2$, obtained by heating benzylic chloride with alcohol and the sodic selenide obtained by reducing sodic selenite with charcoal, forms yellowish scales, which melt at 90° (194° F.); on oxidation by nitric acid it is converted into *benzylselenious acid*, $C_7H_7.SeO.OH$, which crystallizes in white needles, melting at 85° (185° F.). When digested with methylic iodide, it yields benzylic iodide, selenium trimethiodide, and selenium dimethbenzyl triiodide (Jackson):

$$(C_7H_7)_2Se_2 \ + \ 5CH_3I \ = \ C_7H_7I \ + \ (CH_3)_3SeI \ + \ C_7H_7.Se(CH_3)_2I_3.$$

(1619) TELLURIUM ETHERS.—Methylic and ethylic telluride are obtained by distilling potassic telluride with concentrated solutions of methylic and ethylic potassic sulphate. *Methylic telluride*, $(CH_3)_2Te$, is a pale yellow liquid, of intensely disagreeable odour, which boils at about 82° (179°·6 F.); it oxidizes when exposed to the air, forming the compound $(CH_3)_2TeO$. The aqueous solution of this oxide is strongly alkaline to test-paper, and absorbs carbonic anhydride from the air; it displaces ammonia from ammonium salts, and forms a blue precipitate with cupric sulphate. Methylic telluride is violently acted upon by nitric acid; by carefully concentrating the solution, the nitrate $(CH_3)_2Te(OH)NO_3$ may be obtained in crystals. The aqueous solution of this salt yields colourless precipitates of the chloride, $(CH_3)_2TeCl_2$, and bromide $(CH_3)_2TeBr_2$, when mixed with hydrochloric and hydrobromic acid, and when mixed with hydriodic acid, a yellow precipitate of the iodide, $(CH_3)_2TeI_2$, which readily becomes vermilion-red.

Methylic and ethylic telluride combine readily with methylic and ethylic iodides forming compounds analogous to those obtained from the thioethers; the platinochlorides of the corresponding sulphur and tellurium compounds being isomorphous (Cahours).

CHAPTER VIII.

THE ALDEHYDES.

§ I. *The Aldehydes of the* $C_nH_{2n+1}.COH$ *or acetic series;*—§ II. *The Aldehydes of the* $C_nH_{2n-1}.COH$ *or acrylic series;*—§ III. *The Aldehydes of the* $C_nH_{2n-7}.COH$ *or benzoic series;*—§ IV. *Monaldehydes of other series;*—§ V. *Dialdehydes.*

(1620) THE term aldehyde, which is an abbreviation of *alcohol dehydrogenatum*, was originally assigned by Liebig to the compound C_2H_4O, which in 1835 he discovered was the first product of the oxidation of ordinary alcohol, in allusion to its formation from this latter body by the mere withdrawal of hydrogen. It is now applied to all compounds derived in a similar manner from primary carbinols; or, stated more generally, to all compounds containing the group COH (*formyl*), as from the manner in which aldehyde is formed from alcohol, and from its reactions, there can be no doubt that the $CH_2.OH$ group of the alcohol is alone affected and converted by the withdrawal of two atoms of hydrogen into the group COH. The manner in which this withdrawal of hydrogen is probably effected has been discussed on p. 418, where it is pointed out that the alcohol is first transformed by the displacement of one of the atoms of hydrogen in the $CH_2.OH$ group by OH into the dihydric alcohol or aldehydrol (p. 504), which, losing the elements of a molecule of water, is converted into the aldehyde; thus:

$$\underset{\text{Ethylic alcohol.}}{CH_3.CH_2.OH} + (O + OH_2) = \underset{\text{Ethaldehydrol.}}{CH_3.CH(OH)_2} + OH_2;$$

$$\underset{\text{Ethaldehydrol.}}{CH_3.CH(OH)_2} = \underset{\text{Ethaldehyde.}}{CH_3.COH} + OH_2.$$

The general equation for the formation of aldehydes from the corresponding primary carbinols may therefore be written as follows:

$$R^n(CH_2.OH)_n + n(O+OH_2) = R^n[CH(OH)_2]_n + nOH_2;$$

$$R^n[CH(OH)_2]_n = R^n(COH)_n + nOH_2.$$

where R^n denotes a radicle which is n-valent. Hitherto, however, only aldehydes containing one and two COH groups have been prepared, and our knowledge of the latter (*dialdehydes*) is still very imperfect, chiefly the monaldehydes derived from the primary carbinols of the $C_nH_{2n+1}.OH$ and $C_nH_{2n-7}.OH$ series having been investigated. It is scarcely necessary to state that according to the above definition the secondary and tertiary carbinols and phenols cannot furnish aldehydes containing the same number of carbon atoms as themselves, and that the only way, in fact, in which they may be converted into aldehydes is by displacing hydrogen in them by the group COH.

(1621) *Formation of the Aldehydes.*—1. By the oxidation of the primary carbinols, which is usually effected by means of a mixture of potassic dichromate, water and sulphuric acid about in the proportions $K_2Cr_2O_7 : 4H_2SO_4$, and in some cases by dilute nitric acid; for example:

$$\underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2.OH} + (O+OH_2) = \underset{\text{Benzoic aldehyde.}}{C_6H_5.COH} + 2OH_2.$$

$$\underset{\text{Ethylenic alcohol.}}{CH_2.OH.CH_2.OH} + 2(O+OH_2) = \underset{\text{Oxalic aldehyde.}}{COH.COH} + 4OH_2.$$

2. By distilling an intimate mixture of the calcic, potassic, or sodic salt of formic acid and of the acid the aldehyde corresponding to which it is desired to prepare, whereby the OH of the CO.OH group of the acid becomes displaced by H, thus:

$$\underset{\text{Sodic salt of acid.}}{R'.COONa} + \underset{\text{Sodic formate.}}{H.COONa} = \underset{\text{Aldehyde.}}{R'.COH} + \underset{\text{Sodic carbonate.}}{CO(ONa)_2}.$$

$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + H.COONa = \underset{\text{Ethaldehyde.}}{CH_3.COH} + Na_2CO_3.$$

This method has been applied only to the preparation of monaldehydes.

3. By the action of nascent hydrogen on the acid chlorides. For example, on passing hydrogen and benzoic chloride vapour over heated finely divided palladium, benzaldehyde is obtained:

$$C_6H_5.COCl + H_2 = C_6H_5.COH + HCl.$$

Similarly, when phthalic chloride is dissolved in glacial acetic acid and magnesium is added, or when it is digested with zinc and hydrochloric acid, phthaldehyde is formed:

$$C_6H_4(COCl)_2 + 4H = C_6H_4(COH)_2 + 2HCl.$$

The same aldehyde is obtained more readily by the action of hydriodic acid gas in presence of phosphorus on phthalic chloride dissolved in carbonic bisulphide, but this method does not appear to be of general application (Baeyer). The reaction probably takes place in two stages:

$$C_6H_4(COCl)_2 + 2HI = C_6H_4(COI)_2 + 2HCl;$$
$$C_6H_4(COI)_2 + 2HI = C_6H_4(COH)_2 + I_2.$$

The presence of phosphorus has the effect of at once withdrawing the iodine from the sphere of action as it is produced.

4. By heating the chlorinated derivatives of the hydrocarbons of the benzene series of the formula $C_6H_{6-m}(C_nH_{2n}Cl)_m$ with plumbic nitrate and water. This method has been applied to the preparation of benzoic and terephthalic aldehydes.

$$\underset{\text{Paraxylylic chloride.}}{C_6H_4(CH_2Cl)_2} + Pb(NO_3)_2 + OH_2 = \underset{\text{Terephthalaldehyde.}}{C_6H_4(COH)_2} + PbCl_2 + 2HNO_2 + OH_2.$$

5. By treating chlorinated derivatives such as the dichlorotoluene $C_6H_5.CHCl_2$ with concentrated sulphuric acid, and then distilling with water; only benzaldehyde has been prepared by this method, however:

$$C_6H_5.CHCl_2 + 2H_2SO_4 = C_6H_5.CH(HSO_4)_2 + 2HCl;$$
$$C_6H_5.CH(HSO_4)_2 + 2OH_2 = C_6H_5.CH(OH)_2 + 2H_2SO_4;$$
$$C_6H_5.CH(OH)_2 = C_6H_5.COH + OH_2.$$

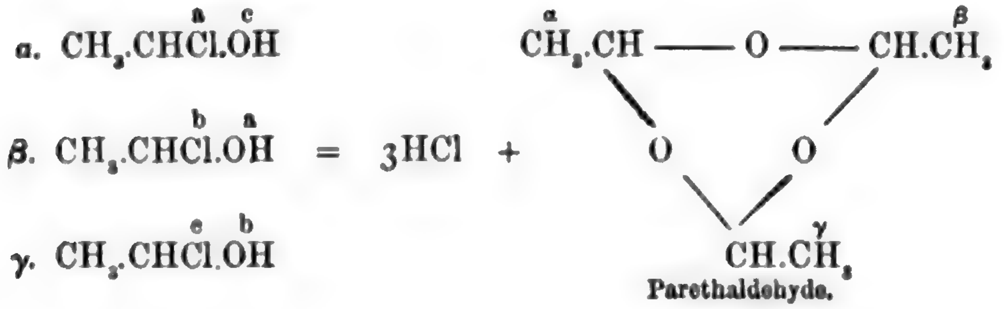
6. By the action of trichloromethane (chloroform) in presence of sodic or potassic hydrate on the phenols (Reimer); the reaction in the case of phenol, which furnishes a mixture of the isomeric orth- and paroxybenzoic aldehydes, may be expressed by the equations:

$$C_6H_5.ONa+3NaOH+CHCl_3=C_6H_4(ONa).CH(OH)_2+3NaCl+OH_2;$$
$$C_6H_4(ONa).CH(OH)_2 = C_6H_4(ONa).COH + OH_2.$$

(1622). *General properties of the Aldehydes.*—1. If pure, the aldehydes may apparently be preserved unchanged for any length of time, but the presence of the merest trace of impurity often suffices to induce their gradual alteration. In some cases, the aldehyde undergoes *polymerization*, that is to say, is converted into a compound or compounds of the same percentage composition but of higher molecular weight; and in others it undergoes *condensation*, two or more molecules uniting with simultaneous elimination of the elements of one or more molecules of water. Thus, if ethaldehyde, C_2H_4O, be mixed with a very small quantity of hydrochloric, sulphurous, or sulphuric acid, or of zincic chloride and of many other salts, the mixture soon becomes heated spontaneously, and the aldehyde is almost entirely converted into a liquid polymeride (*parethaldehyde*) of the composition $C_6H_{12}O_3$; but if the mixture be kept carefully cooled, after some time white needles of another polymeride (*metethaldehyde*) of unknown molecular weight separate from the liquid. On the other hand, if aldehyde be heated with a small quantity of aqueous hydrochloric acid in closed vessels at 100° (212° F.) during several hours, it is in part converted into *crotonic aldehyde*, $C_4H_6O = 2C_2H_4O - OH_2$.

The change appears in both cases to be due to an alteration in the composition of the $(COH)'$ group, which, entering into combination with the agent effecting the change—which may be represented by the general formula $\overset{+}{X}\overset{-}{Y}$, X being the positive and Y the negative radicle—assumes the form $(CH.O\overset{+}{X}.\overset{-}{Y})'$: several molecules of the compound thus generated then either enter into reaction with one another and, in consequence of the separation of X from one molecule in combination with Y from another molecule, form a more complex molecule of the same percentage composition, *i.e.* polymerization takes place; or X and Y separate in combination with hydrogen from a molecule of unaltered aldehyde, the hydrogen being withdrawn from the radicle associated with the COH group, in which case condensation occurs; if X and Y from the same molecule recombine, the aldehyde is reproduced. The formation of parethaldehyde, for example, may be represented in the following manner, it being supposed that the three atoms of chlorine marked a, b, c respectively of the three molecules of the compound $CH_3.CHCl.OH$, formed by the union of the aldehyde with hydrochloric acid, separate in combination with the three atoms of hydrogen marked a, b, c, so that the residue of molecule α unites with that of β, the residue of molecule β with that of γ, and the residue of γ with that of α:

$$\underset{\text{Ethaldehyde.}}{CH_3.COH} + HCl = CH_3.CHCl.OH;$$



Parethaldehyde.

The formation of crotonic aldehyde may be represented in a similar manner by the following equations:

$$CH_3.COH + HCl = CH_3.CHCl.OH;$$
$$CH_3.CHCl.OH + CH_3.COH = CH_3.CH{=}CH.COH + HCl + OH_2.$$

In some cases condensation products are formed by the splitting off of only one of the radicles X or Y from the compound $R'.CH.OX.Y$ in combination with an atom of hydrogen from a molecule of unaltered aldehyde; thus, when a mixture of aldehyde and aqueous hydrochloric acid is allowed to stand for several days *aldol* is produced, the formation of which may be represented by the equations:

$$CH_3.COH + HCl = CH_3.CHCl.OH;$$
$$CH_3.CHCl.OH + CH_3.COH = CH_3.CH(OH).CH_2.COH + HCl.$$

2. The aldehydes are very readily converted by oxidation into corresponding acids, the group COH being converted into the group CO.OH, thus:

$$R'.COH + (O+OH_2) = R'.CO.OH + OH_2.$$
$$\underset{\text{Acetic aldehyde.}}{CH_3.COH} + (O+OH_2) = \underset{\text{Acetic acid.}}{CH_3.COOH} + OH_2.$$

The oxidation may in most cases be effected by mere exposure of the aldehyde to moist air, or by the aid of weak oxidizing agents such as argentic hydrate, but apparently *dry* oxygen (unless in the form of ozone) is entirely without action.

A similar transformation of the aldehydes may be effected by means of fused potassic or sodic hydrate, by the action of which the hydrogen of the COH group is displaced by OK or ONa instead of by OH, the potassic or sodic salt of the acid corresponding to the aldehyde being produced and hydrogen evolved; for example:

$$\underset{\text{Acetic aldehyde.}}{CH_3.COH} + KOH = \underset{\text{Potassic acetate.}}{CH_3.COOK} + H_2.$$

In many cases, however, the hydrogen thus displaced acts upon another portion of the aldehyde, and converts it into the corresponding alcohol; thus:

$$\underset{\text{Benzaldehyde.}}{C_6H_5.COH} + KOH = \underset{\text{Potassic benzoate.}}{C_6H_5.COOK} + 2H;$$
$$\underset{\text{Benzaldehyde.}}{C_6H_5.COH} + 2H = \underset{\text{Benzylic alcohol.}}{C_6H_5.CH_2(OH)}.$$

When heated with an aqueous solution of potassic or sodic hydrate, the aldehydes are mostly converted into resinous substances, which are doubtless also products of condensation.

3. The aldehydes are readily acted on by nascent hydrogen, and converted into the corresponding primary alcohols:

$$R'.COH + 2H = R'.CH_2(OH).$$
$$\underset{\text{Propionic aldehyde.}}{C_2H_5.COH} + 2H = \underset{\text{Propylic alcohol.}}{C_2H_5.CH_2(OH)}.$$

Often, however, the fixation of hydrogen is accompanied by condensation, and in the case of the monaldehydes a dihydric alcohol is produced; thus, if sodium amalgam be added to an aqueous solution of aldehyde, which is maintained slightly acid by repeated additions of hydrochloric acid, ethylic alcohol together with a small quantity of a butylene glycol is produced; the formation of this latter may be represented as the result of several distinct changes:

$$\begin{aligned} CH_3.COH + OH_2 &= CH_3.CH(OH)_2; \\ CH_3.CH(OH)_2 + CH_3.CH(OH)_2 &= CH_3.CH(OH).CH_2.CH(OH)_2 + OH_2; \\ CH_3.CH(OH).CH_2.CH(OH)_2 + 2H &= CH_3.CH(OH).CH_2.CH_2(OH) + OH_2. \end{aligned}$$

4. When submitted to the action of phosphoric pentachloride or pentabromide, the aldehydes exchange their oxygen for the equivalent amount of chlorine or bromine:

$$\begin{aligned} R'.COH + PCl_5 &= R'.CHCl_2 + POCl_3. \\ \underset{\text{Ethaldehyde.}}{CH_3.COH} + PCl_5 &= \underset{\beta\text{-dichlorethane.}}{CH_3.CHCl_2} + POCl_3. \end{aligned}$$

5. By the action of chlorine, they may be converted into the corresponding acid chlorides, the hydrogen of the COH group being displaced by chlorine, but in order to effect this change it is necessary to observe certain precautions in order to avoid the formation of condensation products, or of substitution derivatives; usually the best plan is to add the aldehyde to the chlorine in excess:

$$\begin{aligned} R'.COH + Cl_2 &= R'.COCl + HCl. \\ \underset{\text{Benzoic aldehyde.}}{C_6H_5.COH} + Cl_2 &= \underset{\text{Benzoic chloride.}}{C_6H_5.COCl} + HCl. \end{aligned}$$

6. Sulphuretted hydrogen converts some of the aldehydes into the corresponding thioaldehydes or their polymerides; the formation of these compounds is probably preceded by that of a compound of the aldehyde with sulphuretted hydrogen, which then loses the elements of a molecule of water; thus:

$$\begin{aligned} C_5H_{11}.COH + SH_2 &= C_5H_{11}.CH(SH)(OH); \\ C_5H_{11}.CH(SH)(OH) &= C_5H_{11}.CSH + OH_2. \end{aligned}$$

In some cases compounds intermediate in composition between the aldehydes and the thioaldehydes are perhaps produced, the formation of which may be represented as follows (comp. p. 742):

$$CH_3.COH + SH_2 = CH_3.CH(SH)(OH);$$

$$CH_3.CH(OH)_2 + CH_3.CH(OH)(SH) = CH_3.CH\left\{\begin{matrix}O\\S\end{matrix}\right\}CH.CH_3.$$

7. The aldehydes combine with the acid sulphites of the alkali and alkaline-earthy metals, forming crystalline compounds which are of considerable service in the preparation of the pure aldehydes, as they are decomposed on treatment with a mineral

acid or an alkaline carbonate, or even on warming the aqueous solution, the aldehyde being liberated (comp. 1629):

$$R'.COH + NaHSO_3 = R'.CH(OH).NaSO_3.$$
$$CH_3.COH + NaHSO_3 = CH_3.CH(OH).NaSO_3.$$
$$CH_3.CH(OH).NaSO_3 + OH_2 = CH_3.CH(OH)_2 + NaHSO_3;$$
$$CH_3.CH(OH)_2 = CH_3.COH + OH_2.$$

8. They also combine with cyanic hydride (hydrocyanic acid):

$$R'.COH + HCN = R'.CH(OH).CN.$$
$$\underset{\text{Ethaldehyde.}}{CH_3.COH} + HCN = \underset{\text{Cyanethylic alcohol.}}{CH_3.CH(OH).CN.}$$

By heating the cyanides thus produced with dilute hydrochloric acid, oxyacids are formed, cyanethylic alcohol being converted into ordinary lactic acid:

$$CH_3.CH(OH).CN + 2OH_2 + HCl = CH_3.CH(OH).COOH + NH_4Cl.$$

9. The aldehydes are mostly capable of uniting more or less readily with compounds such as water, hydrochloric acid, monochlorethane (ethylic chloride), C_2H_5Cl, acetic chloride, C_2H_3OCl, acetic anhydride, $(C_2H_3O_2)O$, &c., forming a series of bodies of the form $R.'CH(OX)Y$, which, however, as a rule, are highly unstable, and readily resolved into their generators.

10. They readily enter into reaction with ammonia, apparently combining with it in the first instance in the manner shown by the equation:

$$R'.COH + NH_3 = R'.CH(OH).NH_2.$$

But it is only in the case of the aldehyde of the acetic or $C_nH_{2n+1}COH$ series that the compounds thus formed can be isolated; those derived from aldehydes of other series undergo change more or less rapidly, several molecules entering into reaction with each other to form condensation products. Thus acrylic aldehyde or acrolein, C_2H_3COH, and ammonia yield the compound $C_6H_9NO = 2C_3H_4O + NH_3 - OH_2$; and by the action of ammonia on benzoic aldehyde and other aldehydes derived from hydrocarbons in which the carbon atoms are partially, if not entirely, united in a closed chain, so-called *hydramides* are produced, which are formed by the combination of the elements of two molecules of ammonia and three of aldehyde, the whole of the oxygen of the latter being, however, eliminated in the form of water:

$$\underset{\text{Benzoic aldehyde.}}{3C_6H_5.COH} + 2NH_3 = \underset{\text{Hydrobenzamide.}}{(C_6H_5.CH)_3N_2} + 3OH_2.$$

The compounds formed by the union of the aldehydes of the acetic series with ammonia, such as the so-called aldehyde ammonia, $CH_3.CH(OH).NH_2$, are crystalline substances. They furnish the aldehyde and an ammonic salt on treatment with mineral acids. They enter into reaction with hydrocyanic acid, yielding cyano-derivatives which furnish amido-acids of the acetic series on digestion with hydrochloric or sulphuric acid; thus:

$$\underset{\text{Ethaldehyde.}}{CH_3.COH} + NH_3 = \underset{\text{Amidoethylic alcohol.}}{CH_3.CH(NH_2).OH.}$$

$$\underset{\text{Amidoethylic alcohol.}}{CH_3.CH(NH_2).OH} + HCN = \underset{\text{Cyanamidoethane.}}{CH_3.CH(NH_2).CN} + OH_2.$$

$$\underset{\text{Cyanamidoethane.}}{CH_3.CH(NH_2).CN} + 2OH_2 + HCl = \underset{\text{Amidopropionic acid.}}{CH_3.CH(NH_2).COOH} + NH_4Cl.$$

By the action of dehydrating agents at ordinary temperatures, or on heating either alone or with dehydrating agents, the oxygen they contain is partially or wholly removed in the form of water, ammonia being also split off, and basic condensation products—*oxaldines* and *aldines*—are formed. By the action of sulphuretted hydrogen they are converted into *thialdines*, which may also be formed by digesting the aldehydes with an aqueous solution of ammonic thiohydrate:

$$\underset{\text{Ethaldehyde.}}{3C_2H_4O} + NH_3 + 2SH_2 = \underset{\text{Thialdin.}}{C_6H_{13}NS_2} + 3OH_2;$$

and by the action of carbonic bisulphide they are converted into *carbothialdines*:

$$\underset{\text{Ethaldehyde.}}{2C_2H_4O} + 2NH_3 + CS_2 = \underset{\text{Carbothialdine.}}{C_5H_{10}N_2S_2} + 2OH_2.$$

11. By heating aldehydes with aniline, *phenylated aldines* are produced, the oxygen of the aldehyde being eliminated in the form of water; thus:

$$\underset{\text{Ethaldehyde.}}{CH_3.COH} + 2C_6H_5.NH_2 = CH_3.CH(NH.C_6H_5)_2 + OH_2.$$

$$\underset{\text{Ethaldehyde.}}{CH_3.COH} + 2C_6H_5.NH_2 = CH_3.CH(N.C_6H_5)_2 + OH_2.$$

12. Similarly, by their action on a concentrated aqueous or alcoholic solution of urea, so-called *diureides* are produced:

$$CH_3.COH + 2CO(NH_2)_2 = CH_3.CH(NH.CO.NH_2)_2 + OH_2;$$

whilst if dry urea be employed, still more complex bodies are formed.

13. A reaction of great interest and importance, especially characteristic of the aldehydes derived from hydrocarbons containing the carbon atoms either wholly or partially united in a closed chain, is that which takes place when they are heated with the anhydride of an acid of the acetic series and sodic acetate or the sodic salt of the acid corresponding to the anhydride employed, and the product is subsequently treated with water. The relation of the final product to the aldehyde employed is repre-

sented in the case of benzoic aldehyde and acetic anhydride by the empirical equation:

$$\underset{\text{Benzoic aldehyde.}}{C_6H_5.COH} + \underset{\text{Acetic acid.}}{CH_3.COOH} = \underset{\text{Cinnamic acid.}}{C_6H_5.CH{=}CH.COOH} + OH_2.$$

The reaction does not take place unless the sodic salt is present, but it is scarcely understood at present what part this salt plays; probably, however, the acid is the end product of a series of reactions which occur somewhat in the following manner. In the first place the aldehyde enters into combination with the anhydride; thus, supposing benzoic aldehyde and acetic anhydride are taken:

$$C_6H_5.COH + (C_2H_3O)_2O = C_6H_5.CH(C_2H_3O_2)_2.$$

Condensation then takes place in consequence, it may be supposed, of this compound reacting on a second molecule of the anhydride, two atoms of hydrogen from which separate in combination with the two $C_2H_3O_2$ groups of the diacetin as acetic acid:

$$C_6H_5.CH(C_2H_3O_2)_2 + \left.\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\right\} O = \left.\begin{matrix} C_6H_5.CH{=}CH.CO \\ CH_3.CO \end{matrix}\right\} O + 2C_2H_4O_2.$$

It is undoubtedly at this stage that the sodic salt has an influence; and it perhaps favours the separation of the hydrogen and the formation of the acid in consequence of the tendency exhibited by the acids of the acetic series to combine with their sodic salts to form compounds such as the diacetate, $C_2H_3O_2Na.\ C_2H_4O_2$. Whatever the manner in which condensation is effected, however, there can be little doubt that a mixed anhydride is the product: this is decomposed on the subsequent addition of water, thus:

$$\left.\begin{matrix} C_6H_5.CH{=}CH.CO \\ CH_3.CO \end{matrix}\right\} O + OH_2 = C_6H_5.CH{=}CH.COOH + CH_3.COOH.$$

§ I. ALDEHYDES OF THE $C_nH_{2n+1}COH$ OR ACETIC SERIES.

(1623) The following aldehydes of this series are known:

		B. P. °C.
Methaldehyde or formic aldehyde	$H.COH$	Gaseous
Ethaldehyde or acetic aldehyde	$CH_3.COH$	22°
Propaldehyde or propionic aldehyde	$C_2H_5.COH$	48°·5
Tetraldehyde or butyric aldehyde	$C_3H_7{}^{\alpha}.COH$	75°
Isotetraldehyde or isobutryic aldehyde	$C_3H_7{}^{\beta}.COH$	61°
Pentaldehyde or valeric aldehyde	$C_4H_9{}^{\alpha}.COH$	102°
Isoprimary[*] pentaldehyde or isovaleric aldehyde .	$C_4H_9{}^{\beta}.COH$	93°
Hexaldehyde or caproic aldehyde	$C_5H_{11}{}^{\alpha}.COH$	128°
Isoprimary hexaldehyde or isocaproic aldehyde .	$C_5H_{11}{}^{\beta}.COH$	121°
Heptaldehyde or oenanthic aldehyde	$C_6H_{13}{}^{\alpha}.COH$	152°
Hexdecaldehyde or palmitic aldehyde	$C_{15}H_{31}.COH$	melts at 52°

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[*] The homologues of ethaldehyde, $CH_3.COH$, may be represented as derived from it by the displacement of the hydrogen atoms in the CH_3 group by radicles of the form C_nH_{2n+1}, in precisely the same manner that the alcohols of the ethylic series are regarded as derived from carbinol, $CH_3.OH$; it will be convenient, therefore, to distinguish the three principal classes of homologues of ethaldehyde, and indeed all aldehydes which may be regarded as derived in this way from ethaldehyde, as primary, secondary, and tertiary aldehydes according as they are formed by the displacement of one, two, or three of the hydrogen

(1624) **Methaldehyde, Formic or Methylic Aldehyde**: $CH_2O = HCOH$.—This aldehyde, like the homologous aldehydes, is formed on oxidation of the corresponding alcohol, methylic alcohol, but on account of its properties cannot be directly isolated. If a current of air charged with the vapour of methylic alcohol be directed upon an incandescent platinum spiral, suspended in a glass flask, after a few minutes the flameless combustion of the alcohol begins to manifest itself by the evolution of a vapour powerfully affecting the eyes and nose; if the current of air be properly adjusted, the spiral remains incandescent for hours and even for days, and by passing the vapour through a well-cooled condenser and wash bottles, a product having all the properties characteristic of the aldehydes is obtained. Thus, when it is rendered slightly alkaline by ammonia, and gently warmed with argentic nitrate, silver is deposited on the sides of the vessel; and on heating it with potassic hydrate, it acquires a yellowish colour, and soon deposits drops of a brownish oil possessing the peculiar odour of ethaldehyde resin. In all probability the solution contains methaldehydrol, $CH_2(OH)_2$, but on evaporation over sulphuric acid in vacuo, instead of this compound, or the aldehyde derived from it by the simple withdrawal of the elements of a molecule of water, there is obtained a small quantity of a yellowish-white substance, which is a polymeride of methaldehyde. There can be little doubt, however, that this polymeride is not contained in the solution, as it is insoluble in water, and has but a faint odour, whereas the solution is miscible with

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atoms, and to employ the terms isoprimary, isosecondary, &c., in the same sense as in the case of the carbinols to represent aldehydes containing radicles other than normal—*i.e.*, in which the carbon atoms are supposed to be united in a manner different from that in which they are in the normal paraffins. Thus:

$CH_3.OH$ Carbinol.	$CH_2R'.OH$ Primary carbinol.	$CHR'_2.OH$ Secondary carbinol.	$CR'_3.OH$. Tertiary carbinol.
$CH_3.COH$ Ethaldehyde.	$CH_2R'.COH$ Primary aldehyde.	$CHR'_2.COH$ Secondary aldehyde.	$CR'_3.COH$. Tertiary aldehyde.

It may be objected that on this system the aldehydes would have to be regarded as derivatives of a compound containing two atoms of carbon, whereas the carbinols are derivatives of a compound containing only a single carbon atom. Ethaldehyde and carbinol, however, may obviously both be regarded as formed in a similar manner from methane, CH_4, by the displacement of a single atom of hydrogen by the monad radicles OH and COH; in fact the object is simply to indicate the nature of the radicle associated with the OH and COH groups, and the most convenient way of doing this is to term those compounds primary which contain a radicle of the form $(CH_2R')'$, and to apply the terms secondary and tertiary respectively to all those which contain radicles of the form $(CHR'_2)'$ and $(CR'_3)'$.

water and smells strongly (Hofmann, *Proc. Roy. Soc.*, xv. 156; *Deut. chem. Ges. Ber.*, ii. 152; iii. 584).

Hofmann has recently stated that methylic alcohol can be oxidized with great facility by passing its vapour mixed with air through a platinum tube packed with platinum wire, which is gently heated in the first instance in order to start the reaction.

The formation of methylal (p. 680), $CH_2(OCH_3)_2$, on oxidation of methylic alcohol by a mixture of sulphuric acid and manganic dioxide, and of dimesitylmethane (1380), $CH_2(C_9H_{11})_2$, on adding mesitylene, $C_6H_3(CH_3)_3$, to a mixture of solutions of methylic alcohol and of chromic anhydride in glacial acetic acid, indicates also that ordinary oxidizing agents convert methylic alcohol into the corresponding aldehyde.

The preparation of methaldehydrol from diiodomethane, and its conversion into the polymeride of methaldehyde, has already been described (1495). The latter compound is also formed by the action of argentic oxalate or argentic oxide on diiodomethane (Butlerow, *Ann. Chem. Pharm.*, cxi. 245); probably the best method of preparing it, however, is to heat the calcic salt of glycolic acid, $CH_2(OH).COOH$, with six or eight times its weight of concentrated sulphuric acid.

The calcic salt previously dehydrated by heating at 190° (374° F.), is introduced into a capacious retort together with the acid, and the decomposition into calcic sulphate and glycolic acid effected by gently warming the mixture and constantly agitating the retort; a thermometer is then immersed in the liquid, and the head of the retort covered over with paper so as to prevent condensation. The neck of the retort is connected with a receiver, a wide glass tube being fitted to the other neck of the receiver. The mixture is then heated with moderate rapidity to a temperature of 170°—180° (338°—356° F.), so that the product as it is formed at once sublimes into the neck of the retort; but the heating must not take place too rapidly, as in this case the carbonic oxide which is abundantly evolved carries with it a large quantity of the methaldehyde which thus escapes condensation (Heintz, *Ann. Chem. Pharm.*, cxxxviii. 40).

According to Brodie, a small quantity of methaldehyde is produced when a mixture of hydrogen and carbon dioxide gases is submitted to the action of the silent electric discharge (*Proc. Roy. Soc.* 1874, xxii. 171). P. and A. Thenard state that when a mixture of hydrogen and carbonic oxide is similarly treated, it yields a liquid product soluble in water, which exhibits strong reducing properties (*Compt. Rend.*, lxxvi. 1049).

The polymeride of methaldehyde is an amorphous, tasteless substance, almost destitute of odour, but when heated it gives off vapour having a very pungent, irritating odour; it begins to sublime below 100° (212° F.) without melting, but if rapidly heated it melts at 152° (305°·6 F.), and at the same time boils.

When thus volatilized, it is depolymerized, its vapour density corresponding with the formula CH_2O (Hofmann). If the density be determined in Hofmann's apparatus, it is observed, however, that the mercury does not at once rise to its former level when the apparatus becomes cold, as is ordinarily the case, and that it only very slowly regains its former level: the gaseous methaldehyde being but gradually reconverted into the solid polymeride.

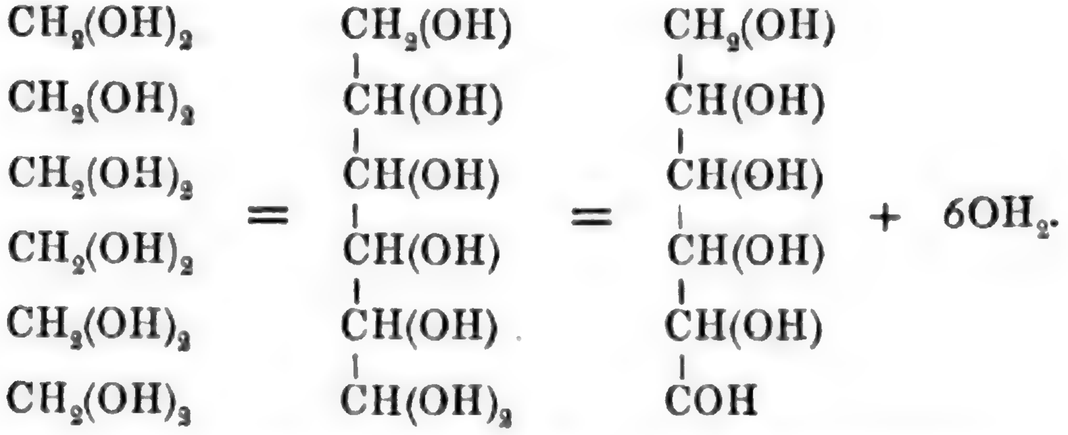
If the methylic alcohol solution of (?) methaldehydrol be mixed with ammonia and then evaporated in vacuo, ***hexmethylenamine***, a crystalline body of the composition $C_6H_{12}N_4 = 6CH_2(OH)_2 + 4NH_3 - 12OH_2$ is obtained; this compound is also formed when the solid polymeride of methaldehyde is submitted to the action of dry ammonia gas. It crystallizes from alcohol in colourless, transparent rhombohedra and prisms, easily soluble in water and in hot alcohol. It is odourless at ordinary temperatures, but when heated emits a most unpleasant odour. It slowly sublimes at about 100° (212° F.), condensing in well-formed, brilliant crystals. Hexmethylenamine combines with acids forming salts such as the hydrochloride $C_6H_{13}N_4Cl$ (Butlerow, *Ann. Chem. Pharm.*, cxv. 322).

If a current of sulphuretted hydrogen be passed through the methylic alcohol solution of methaldehydrol, the liquid becomes turbid after a few minutes, and on allowing the saturated solution to stand for some hours a body of an alliaceous odour begins to be separated at the bottom of the flask. If the liquid be now mixed with half its volume of concentrated hydrochloric acid and heated to ebullition, it becomes limpid and solidifies on cooling into a mass of felted needles of *thiomethaldehyde*; the solid polymeride of methaldehyde also furnishes this compound on treatment with sulphuretted hydrogen and hydrochloric acid (Hofmann). Moreover, it may be obtained by digesting carbonic bisulphide with zinc and hydrochloric acid (Girard, *Compt. Rend.*, xliii. 396), and from diiodomethane: when the last-mentioned compound is warmed with an alcoholic solution of sodic sulphide, a white, voluminous, amorphous precipitate of a substance of the composition xCH_2S is formed, and on heating this at about 150° (302° F.) it becomes crystalline, and then has all the properties of the thioaldehyde prepared as above described. Thiomethaldehyde is also a product of the action of nascent hydrogen on thiocyanic acid, HCNS, and on allylic isothiocyanate, $C_3H_5.NCS$ (Hofmann, *Deut. chem. Ges. Ber.*, i. 176). It melts at 218° (424°·4 F.), and may be volatilized unchanged; the determination of its vapour density shows that it has the formula $C_3H_6S_3$. It forms crystalline compounds with argentic nitrate—viz., $C_3H_6S_3.AgNO_3$ and $C_3H_6S_3.2AgNO_3$—and with a number of metallic chlorides.

It appears probable from the high melting point of the polymeride of methaldehyde, and from the readiness with which it is converted into the thioaldehyde $C_3H_6S_3$, that it also is formed from three molecules of methaldehyde.

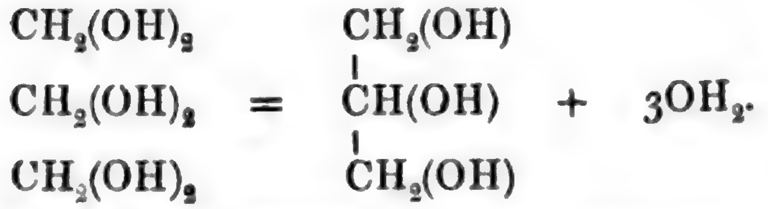
Baeyer has shown that when methaldehyde acts on benzene and the homologous hydrocarbons, and on bodies such as phenol, in presence of dehydrating agents such as sulphuric and hydrochloric acids, condensation products are obtained which are formed by the separation of the oxygen of the aldehyde in combination with hydrogen of the body acted upon; thus, when it acts upon benzene, a mixture of diphenylmethane or benzylbenzene (1377), $CH_2(C_6H_5)_2$, and paradibenzylbenzene (1403), $C_6H_4(CH_2.C_6H_5)_2$, and which even contains still more complex hydrocarbons, is obtained (comp. p. 359). Methaldehyde acts on mesitylene in this manner so readily, and the product (1380) has such characteristic properties, that the reaction may be made use of for its detection.

There can be little doubt that methaldehyde, or more probably methaldehydrol, is one of the first, if not the first and only reduction product formed from the carbonic acid in plants, and in virtue of this property of readily entering into reaction with other bodies in the manner described, it doubtless plays a most important part in plant life in effecting the gradual building up of many of the complex compounds which are products of vegetable organisms. The formation of dextrose, for example, may be regarded as simply the result of the action upon each other of six molecules of methaldehydrol and the separation from them of the elements of six molecules of water, thus:



$$\begin{array}{l} \mathrm{CH_2(OH)_2} \\ \mathrm{CH_2(OH)_2} \\ \mathrm{CH_2(OH)_2} \\ \mathrm{CH_2(OH)_2} \\ \mathrm{CH_2(OH)_2} \\ \mathrm{CH_2(OH)_2} \end{array} = \begin{array}{l} \mathrm{CH_2(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)_2} \end{array} = \begin{array}{l} \mathrm{CH_2(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{COH} \end{array} + 6\mathrm{OH_2}.$$

That of glycerol may be represented in a similar manner:



$$\begin{array}{lcl} CH_2(OH)_2 & & CH_2(OH) \\ & & \quad | \\ CH_2(OH)_2 & = & CH(OH) \quad + \quad 3OH_2. \\ & & \quad | \\ CH_2(OH)_2 & & CH_2(OH) \end{array}$$

Obviously the changes involved in these reactions are precisely analogous to those which there is every reason to suppose take place for example, in the formation of butylene glycol and of crotonic aldehyde, from ethaldehyde (pp. 717—719). It is by no means improbable that some at least of the metallic salts which are requisite for plant growth assist in bringing about these changes, and hence are necessary to growth, although they do not form part of the plant structure, as it has been placed beyond doubt that whereas pure ethaldehyde may be preserved unchanged; if a minute quantity of a foreign substance be added, it rapidly undergoes polymerization and condensation. The necessity of the presence of potassic salts in the formation of starch, for example, may thus meet with an explanation.

(1625) ETHALDEHYDE; ACETIC or ETHYLIC ALDEHYDE; ALDEHYDE: $C_2H_4O=CH_3.COH$.—This aldehyde is a product of the action of nearly every oxidizing agent on ethylic alcohol. Oxygen alone, however, unless in the form of ozone, is incapable of converting alcohol into aldehyde at ordinary temperatures, although in the presence of platinum black action readily takes place: many other substances facilitate the oxidation in a similar manner, aldehyde being even produced on merely filtering alcohol through charcoal (Krämer and Pinner); and certain of the minute organisms which excite fermentation appear to possess the power of inducing the oxidation of alcohol, for aldehyde is sometimes met with as a product of vinous fermentation, especially when it takes place under reduced pressure, and in acetous fermentation. The oxidation of alcohol may also be effected by passing the vapour mixed with air through a platinum tube packed with platinum wire which only at first requires to be gently heated, the heat developed in the formation of the aldehyde being then sufficient to maintain the temperature high enough for the oxidation of the alcohol to take place continuously. In all these cases in which aldehyde is produced by oxidation of alcohol, the reaction may with much probability be supposed to take place in the following manner:

$$\underset{\text{Ethylic alcohol.}}{CH_3.CH_2.OH} + (O+OH_2) = \underset{\text{Ethaldehydrol.}}{CH_3.CH(OH)._2} + OH_2.$$

$$\underset{\text{Ethaldehydrol.}}{CH_3.CH(OH)_2} = \underset{\text{Ethaldehyde.}}{CH_3.COH} + OH_2.$$

It is obtained in small quantity on oxidation of many other substances besides alcohol, especially complex bodies, such as the carbohydrates and albuminoids, and when the vapour of alcohol or of ether is passed through a tube heated to dull redness; it is also one of the products of the dry distillation of bodies such as sugar, and of wood. The following are other methods of forming aldehyde:—(*a*) By combining acetylene with sulphuric acid, and decomposing the product with water; the aldehyde thus formed, however, as Lagermarck and Eltekoff have recently shown (*Deut. chem. Ges. Ber.*, x. 637), becomes converted into crotonic aldehyde. It was stated by Berthelot that vinylic alcohol was produced in this manner, but it has already been pointed out (p. 213) that the substance he obtained was in all probability crotonic aldehyde; Lagermarck and Eltekoff's observations leave little doubt that the explanation previously given of the formation of this compound from acetylene is correct. (*b*) (?) By the action of a concentrated aqueous solution of chromic acid on ethylene at 120° (248° F.) (Berthelot). (*c*) By heating α- or β-dibromethane (ethylenic and ethylidenic bromides) with water or alcohol in closed tubes at 150°—170° (302°—338° F.); when water is employed, a great part of the aldehyde is converted into a resinous substance, the formation of which is avoided if alcohol be taken (Carius, *Ann. Chem. Pharm.*, cxxxi. 17; *comp.* 511). It may also be formed from β-dibromethane, $CH_3.CHBr_2$, by converting the latter into acetal by the action of sodic ethylate (*comp.* p. 680), and heating this compound with acetic acid at 150° (302° F.):

$$CH_3.CH(OC_2H_5)_2 + 2HC_2H_3O_2 = CH_3.COH + OH_2 + 2C_2H_5.C_2H_3O_2.$$

(*d*) By the action of zincic chloride on glycol (Wurtz). On adding glycol to powdered fused zincic chloride, heat is developed, and a portion of the chloride is dissolved. If a mixture of 1 pt. glycol and 3 pts. zincic chloride be heated in the oil bath at about 250° (482° F.) a moderately vigorous reaction takes place, and vapours pass off, which, when condensed, form two layers—an upper oily layer, consisting of hydrocarbons, and a lower aqueous layer, containing ethaldehyde and a second substance, boiling, according to Bauer, at 105°—110° (221°—230° F.), which is doubtless crotonic aldehyde. (*e*) By heating fermentation lactic acid for several hours at about 130° (266° F.) with dilute sulphuric acid (Erlenmeyer):

$$CH_3.CH(OH).COOH + OH_2 = CH_3.CH(OH)_2 + H.COOH.$$

It is also formed in small quantity when lactic acid and many of its salts are submitted to dry distillation. (*f*) By distilling a mixture of calcic formate and calcic acetate:

$$(HCOO)_2Ca + (CH_3.COO)_2Ca = 2CH_3.COH + 2CaCO_3.$$

(*g*) By passing chlorine into aqueous alcohol; the formation of ethaldehyde by this reaction may be explained in two ways: it may either be supposed that by the action of the chlorine on the water oxygen is liberated, which then oxidizes the alcohol: $CH_3.CH_2.OH + OH_2 + Cl_2 = 2HCl + CH_3.COH + OH_2$; or, which is more probable, that a chlorinated derivative of alcohol is formed, which splits up into ethaldehyde and hydrochloric acid:

$$CH_3.CH_2.OH + Cl_2 = CH_3.CHCl.OH + HCl;$$
$$CH_3.CHCl.OH = CH_3.COH + HCl.$$

(*h*) According to Saytzeff and Glinsky (*Zeits. Chem* [2], iii. 645), ethaldehyde and a compound of ethaldehyde and mercurous bromide are obtained on digesting bromethylene, $CH_2{=\!=}CHBr$, with crystallized mercuric acetate.

Preparation.—Ethaldehyde is usually prepared by oxidizing ethylic alcohol with potassic dichromate, or manganic dioxide, and sulphuric acid. The following method may be advantageously employed:

Fifteen parts of potassic dichromate in pieces the size of small pease is placed in a capacious retort surrounded by ice and salt, and a cold mixture of ten parts spirits of wine and twenty parts concentrated sulphuric acid diluted with three times its volume of water is then poured in. The retort is connected with a reversed Liebig's condenser, or with a spiral, which is connected by glass tubing with two cylinders, one of which—that nearer to the condenser—is empty, the other being partially filled with anhydrous ether; water of about 50° (122° F.) is allowed to flow through the condenser, and the cylinders are surrounded by a refrigerating mixture of ice and salt. The reaction begins on removing the refrigerating mixture surrounding the retort, the liquid in which boils violently; after a time, however, it is necessary to heat the retort gently in order to complete the oxidation. The aldehyde distils over and collects in the two receivers, while the vapours of alcohol and of the oxidation products formed simultaneously with the aldehyde (ethylic acetate, acetic acid, &c.) which also volatilize are in a great measure condensed, and flow back into the retort. In order to obtain pure ethaldehyde, the ethereal solution is saturated with ammonia gas, and the compound of ethaldehyde with ammonia which separates out is washed with ether, dried over sulphuric acid, then dissolved in a small quantity of water, mixed with dilute sulphuric acid, and the mixture carefully distilled from the water bath; the distillate is dried over calcic chloride and then rectified.

Instead of adding the mixture of alcohol and acid to the dichromate, the latter may be dissolved in the acid and water, and the alcohol gradually added to the solution by means of a funnel provided with a stopcock passing through the tubulus of the retort; it is not necessary in this case to cool the retort. Instead also of collecting the aldehyde in ether, it may be collected alone in well cooled receivers, and partially purified by rectification; but it is impossible to purify it completely by fractional distillation.

On rectifying crude fermentation spirit which has passed through charcoal filters, a portion passes over almost immediately when steam is first blown into the stills consisting chiefly of ethaldehyde; about two quarts of this highly volatile fraction are obtained from 30,000 quarts of spirit (Krämer and Pinner, *Deut. chem. Ges. Ber.*, ii. 401; iv. 787). This commercial product is now the most convenient source of ethaldehyde, which may be prepared from it in a pure state, by means of the compound with ammonia.

Properties.—Ethaldehyde is a colourless, very mobile, inflammable liquid, possessing a characteristic pungent not unpleasant smell; when inhaled it produces a peculiar sensation of tightness at the chest. It boils at 22° (71°·6 F.), and at 0° (32° F.) has the sp. gr. 801. It is miscible with water, alcohol, and ether in all proportions, dissolving in water and alcohol with considerable development of heat, doubtless owing to the formation of the compounds $CH_3.CH(OH)_2$ and $CH_3.CH(OH)(OC_2H_5)$.

The aqueous solution is perfectly neutral, but soon becomes acid in consequence of the production of acetic acid, $CH_3.COOH$; this acid is formed with the greatest facility from ethaldehyde, by the action of all oxidizing agents. Thus, on warming an aqueous solution of ethaldehyde with argentic oxide, the latter is reduced to the metallic state, the aldehyde being converted into argentic acetate; similarly, when the solution formed by adding ammonia to a solution of argentic acetate, until the precipitate at first produced is redissolved, is gently warmed with ethaldehyde, the following reaction takes place:

$$CH_3.CH(OH)_2 + 2AgNH_2.OH = 2Ag + CH_3.COONH_4 + NH_3 + 2OH_2.$$

The silver separates in the form of a brilliant mirror on the sides of the flask or tube in which the liquid is heated; this reaction is extremely delicate, and may be made use of for the detection of ethaldehyde.

It is not reduced in contact with zinc and hydrochloric acid, but on adding sodium amalgam to an aqueous solution of ethaldehyde, ethylic alcohol is produced; it is advisable to maintain the solution faintly acid by adding hydrochloric acid from time to time in order to prevent the formation of resinous compounds by the action of the alkali (Wurtz). According to Kekulé, a small quantity of the glycol $CH_3.CH(OH).CH_2.CH_2(OH)$ is produced simultaneously (*comp.* 1500). Ethaldehyde is also converted into ethylic alcohol by digesting its solution in aqueous ammonia with zinc at 30°—40° (86°—104° F.) under slight pressure; basic substances are apparently formed at the same time (Lorin, *Compt. Rend.*, lvi. 845).

Ethaldehyde is readily acted upon by phosphoric pentachloride and trichlorodibromide, being converted into β-dichlor- and β-dibromethane (ethylidenic chloride and bromide), $CH_3.CHCl_2$ and $CH_3.CHBr_2$. According to Tawildarow (*Deut. chem. Ges. Ber.*, vii. 488), the latter compound is not obtained by the action of phosphoric pentabromide on ethaldehyde, the product in this case being the compound $CH_3.CHBr(C_2H_3O_2)$, which may also be obtained by combining ethaldehyde with acetic bromide. On heating it with a solution of potassic or sodic hydrate the liquid becomes coloured in consequence of the formation of so-called *aldehyde-resin,* a brown amorphous substance of unknown composition, but which is doubtless a product of condensation.

When the vapour of ethaldehyde is passed over lime heated to dull redness, acetone, $CO(CH_3)_2$, and homologous compounds are produced (Schlömilch).

(1626) *Polymerization of Ethaldehyde.*—A number of polymerides of ethaldehyde have at various times been described, but it has been shown by Kekulé and Zincke (*Ann. Chem. Pharm.*, clxii. 141) that only two exist—viz., *metethaldehyde,* which is crystalline, and *parethaldehyde,* which is liquid, at the ordinary temperature; both may be formed by the action of the same substances on ethaldehyde, but the former is produced at low and the latter at higher temperatures.

Parethaldehyde; paraldehyde: $C_6H_{12}O_3$.—A large number of substances possess the power of converting ethaldehyde into this polymeride; thus, if a very minute quantity of hydrochloric or sulphurous acid, or of carbonic chloride, $COCl_2$, be added to ethaldehyde, the temperature very soon rises and may even reach 38°—40° (100°·4—104° F.) if the reaction takes place in a closed vessel, the greater part of the aldehyde being converted into parethaldehyde. On the addition of a drop of concentrated sulphuric acid to ethaldehyde, boiling at once sets in with explosive violence, and much of the aldehyde is volatilized; the residue consists of parethaldehyde. Diluted acid acts less violently. Zincic chloride has a similar action, but calcic chloride and potassic acetate do not produce parethaldehyde, and acetic acid appears to be entirely without action. The paraldehyde is best purified by submitting the crude product to a temperature below 0° (32° F.) for some time; it then crystallizes out, and may be freed from the liquid by pressure between folds of bibulous paper, and distilled. It is a colourless liquid, of pleasant ethereal odour, soluble to the extent of about 12 vols. in 100 vols. of water at 13° (55°·4 F.); it solidifies below 10° (50° F.) to an ice-like mass, but sometimes forms large transparent prisms; the crystals melt at 10°·5 (50°·9 F.). It boils at 124° (255°·2 F.), and at 15° (59° F.) has the sp. gr. 998. Its vapour density corresponds to the formula $C_6H_{12}O_3$. When distilled with a small quantity of sulphuric or hydrochloric acid, or with zincic chloride, &c., it is reconverted into ethaldehyde; it also furnishes the same products as ethaldehyde when acted upon by phosphoric pentachloride or hydrochloric acid gas, the former converting it into β-dichlorethane, and the latter into the dichlorether, $CH_3.CHCl.O.CHCl.CH_3$ (p. 672).

Metethaldehyde; metaldehyde: xC_2H_4O.—This polymeride separates in long fine needles when, after the addition of a small quantity of any of the substances which are capable of converting ethaldehyde into parethaldehyde, the liquid is well cooled; the amount formed, however, is always small, and does not increase on standing. The best method of preparing it is to pass a few bubbles of hydrochloric acid or sulphurous anhydride into the pure aldehyde, and then to cool it by ice, or still better, by a mixture of ice and salt; after an hour or so the crystals are separated by filtration, and the residue is distilled with a small quantity of sulphuric acid, the distillate being collected in a well-cooled receiver. A fresh quantity of metethaldehyde then forms in the distillate, and a considerable quantity may be prepared if these operations are repeated sufficiently often; sometimes it is desirable to add a further small quantity of the substance originally employed to effect the change to the distillate, or to distil nearly to dryness, which produces a sufficient amount of sulphurous anhydride. Crystals of metethaldehyde often form on pieces of calcic chloride placed in pure ethaldehyde.

Metethaldehyde appears to crystallize in forms belonging to the quadratic system. When rapidly heated, it suddenly sublimes in small needles. When thus sublimed, however, a portion undergoes conversion into ethaldehyde, and it may be entirely depolymerized by heating at 112°—115° in closed tubes for several hours. It is insoluble in water, and only slightly soluble in cold alcohol, benzene, or ether; it is somewhat more soluble in the hot liquids, and crystallizes out in long needles as the solutions cool. When it is warmed with a small quantity of dilute sulphuric acid, pure ethaldehyde distils over; in presence of a small quantity of hydrochloric acid gas, it gradually disappears, furnishing a mixture of ethaldehyde and parethaldehyde. Phosphoric pentachloride converts it into β-dichlorethane. It is not altered by heating with ammonia at 120° (248° F.) (Krämer and Pinner).

The manner in which the paraldehyde and metaldehyde are probably formed from ethaldehyde has already been explained (p. 717), where the constitution of the former has also been indicated. At present there are no data which enable us to decide what is the molecular weight of metethaldehyde, but as it is less fusible and also less soluble, as well as less stable than parethaldehyde, it has probably a higher molecular weight than the latter.

(1627) *Condensation of Ethaldehyde.*—Pure ethaldehyde is not altered when heated alone or with water at 100° (212° F.), but if a mere trace of hydrochloric or sulphuric acid or of zincic chloride be present, the aldehyde is converted chiefly into crotonic aldehyde (q. v.), $C_4H_6O = CH_3.CH{=\!=}CH.COH$; the same change takes place at ordinary temperatures, although much more slowly, and many salts and other substances besides those mentioned induce condensation. Besides crotonic aldehyde, higher condensation products are formed, especially if the heating be long continued, but these have not yet been obtained in a pure state (Kekulé, *Ann. Chem. Pharm.*, clxii. 196).

If well-cooled ethaldehyde be saturated with hydrochloric acid gas, the latter is at first absorbed, but after a time two layers are formed, one being an aqueous solution of hydrochloric acid, and the other the dichlorether $(CH_3.CHCl)_2O$. If the latter be allowed to remain in contact with the acid, it rapidly undergoes change, becoming brown and after a time completely resinified (Baeyer). One of the products of this change is crotonic aldehyde, and a second is a crystalline chlorobutyric aldehyde, $C_3H_6Cl.COH$, formed apparently by the combination of the crotonic aldehyde with hydrochloric acid; sometimes a crystalline compound of the formula $C_{10}H_{13}Cl_2O_3$ is also obtained (Kekulé).

If, however, 1 pt. of ethaldehyde be mixed with 1 pt. of water and 2 pts. of a saturated solution of hydrochloric acid, and the mixture be left to itself for several days at a temperature of 15°—20° (59°—68° F.), *aldol* or *oxybutyric aldehyde* (q. v.), $C_4H_8O_2 = CH_3.CH(OH).CH_2.COH$, is produced (Wurtz).

Hydriodic acid also readily acts on ethaldehyde with separation of water and formation of condensation products, which have not yet been examined, however (Geuther and Cartmell, *Ann. Chem. Pharm.*, cxii. 16). According to Berthelot, ethane is produced when ethaldehyde is heated with hydriodic acid at high temperatures.

On passing trimethylamine into an ethereal solution of ethaldehyde, water separates, and condensation products are formed (Lubavin, *Deut. chem. Ges. Ber.*, viii. 1684).

Riban (*Compt. Rend.*, lxxv. 98) states that sodium dissolves in an ethereal solution of ethaldehyde with evolution of hydrogen, and that if hydrochloric acid gas be then passed into the liquid until it is slightly acid, and it be subsequently evaporated, &c., ethaldol is obtained; but from Borodin's experiments on isopentaldehyde (*Deut. chem. Ges. Ber.*, v. 480) it appears probable that the hydrogen evolved cannot have been derived from the aldehyde, and that the alteration of the latter was caused by the sodic hydrate or ethylate formed from the water or alcohol present in the ether. Riban also obtained condensation products of ethaldehyde by heating it with zinc turnings at 100° (212° F.).

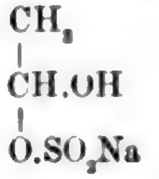
(1628) *Action of Chlorine and Bromine on Ethaldehyde.*—The nature of the product obtained by the action of chlorine on ethaldehyde depends on the conditions of experiment. Thus, when ethaldehyde is poured into glass flasks filled with chlorine, *acetic chloride*, $CH_3.COCl$, and the chloracetin of aldehydrol, $CH_3.CHCl.OC_2H_3O$, are the chief products; these substances are also formed on passing chlorine into an ice-cold mixture of tetrachloromethane with one-tenth of its weight of ethaldehyde in sunshine (Wurtz, *Compt. Rend.*, lxxiii. 528). If, however, a well-cooled aqueous solution of the aldehyde be submitted to the action of chlorine, trichlorethaldehydrol or chloral-hydrate, $CCl_3.CH(OH)_2$, is the final product: but in this case we must assume that ethaldehydrol, $CH_3.CH(OH)_2$, and not ethaldehyde, $CH_3.COH$, is acted upon, and hence the difference in the results. On passing chlorine into ethaldehyde cooled to −10° (14° F.), the gas is entirely absorbed, but after a time the liquid becomes filled with needles of metethaldehyde; on continuing to pass the chlorine, a colourless, heavy liquid, consisting of an aqueous solution of hydrochloric acid, collects at the bottom of the vessel, and finally a yellow or brownish syrupy mass more than double the weight of the aldehyde taken is obtained, very little hydrochloric acid being evolved. Parethaldehyde furnishes a precisely simiiar product, but is much less violently acted on. In this manner the ethaldehyde is finally converted into trichlorotetraldehyde, $C_3H_4Cl_3.COH$ (Krämer and Pinner; Pinner, *Ann. Chem. Pharm.*, clxxix. 21), the formation of which, however, is undoubtedly the end result of a long series of changes: in the first place a certain quantity of acetic chloride is probably produced, but the hydrochloric acid liberated in its formation rapidly induces the conversion of the aldehyde in part into polymerides and in part into crotonic aldehyde; later on, however, these polymerides doubtless also undergo conversion into crotonic aldehyde, under the influence of the hydrochloric acid. The crotonic aldehyde thus produced then either combines with hydrochloric acid, forming a chlorotetraldehyde, which is acted upon by the chlorine and further chlorinated; or it combines with chlorine, and the resulting dichloraldehyde is converted into trichloraldehyde by the further action of the chlorine; or it becomes partially chlorinated, and then unites either with hydrochloric acid or chlorine. The water produced in the formation of the crotonic aldehyde doubtless plays a useful part in preventing the formation of acetic chloride, or of chlorides corresponding to the aldehydes produced, by combining with these latter, so that really the aldehydrols and not the aldehydes are acted upon by chlorine.

Bromine acts even more violently than chlorine on ethaldehyde, and in order therefore to examine its action it is necessary to dilute the aldehyde; but parethaldehyde being less violently acted upon is more conveniently employed. When bromine is carefully added to a well-cooled solution of parethaldehyde in two or three times its weight of carbonic bisulphide, the reaction appears to take place in precisely the same way as when chlorine is employed, hydrobromic acid being evolved, while water is seen to separate; but on distilling the product it is entirely decomposed. If, however, ethylic acetate be employed as diluent, the di- and tri-brominated derivative of ethaldehyde are readily produced; apparently monobromethaldehyde cannot be prepared in this manner, the product obtained on adding bromine to a solution of ethaldehyde in the requisite proportions being entirely decomposed on distillation (Pinner, *loc. cit.*, p. 67). Iodine is dissolved by ethaldehyde, but apparently is without action upon it.

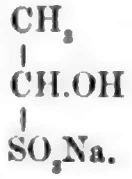
(1629) *Combination of Ethaldehyde with Acid Sulphites.*—Ethaldehyde dissolves in a concentrated solution of hydric potassic sulphite with considerable development of heat, and if the clear solution be concentrated over sulphuric acid, the compound $CH_3.CH(OH).SO_3K$ is obtained as a hard crystalline mass consisting of needles grouped together in bundles. This salt may be preserved unchanged under ordinary conditions, but is decomposed at 100° (212° F.), and also on heating its aqueous solution; in the latter case ethaldehyde and sulphurous anhydride are given off, potassic sulphite remaining in solution. It is also decomposed by alkaline carbonates, with formation of ethaldehydrol and a normal sulphite.

The corresponding sodium compound is prepared in a similar manner; it is extremely soluble in water, crystallizing from the solution on slow evaporation in glistening plates of the composition $2CH_3.CH(OH).NaSO_3 + OH_2$. The barium compound, $(CH_3.CH(OH).SO_3)_2Ba$, may be prepared by adding a slight excess of ethaldehyde to a solution of sulphurous acid, then neutralizing with baric carbonate, and adding alcohol to the clear solution, when it is thrown down as a glistening precipitate. The aqueous solution of this salt is decomposed by boiling, either alone or with sodic carbonate or baric hydrate, but it is not altered by carbonic or sulphurous acids.

These compounds of ethaldehyde (and of its homologues) with the acid sulphites may be regarded either as derivatives of sulphurous or of sulphuric acid, thus:

I. 

$$\begin{matrix} CH_3 \\ | \\ CH.OH \\ | \\ O.SO_2Na \end{matrix}$$

II. 

$$\begin{matrix} CH_3 \\ | \\ CH.OH \\ | \\ SO_3Na. \end{matrix}$$

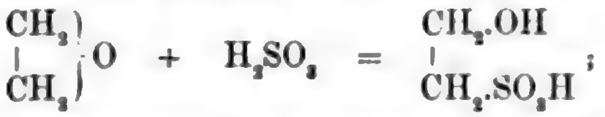
Their slight stability would appear to favour the former assumption, but there is evidence of the latter being the more probable. Thus when β-dichlorethane, $CH_3.CHCl_2$, is heated with a solution of sodic sulphite in sealed tubes at about 140° (284° F.), one half the chlorine is displaced by the group SO_3Na, and the sodic salt of a body which from its behaviour is undoubtedly a sulpho-acid is produced; but this is not the only product of the reaction: the contents of the tubes exhibit an acid reaction and smell of sulphurous acid, the more so the higher the temperature to which it has been heated and the longer the heating has been continued, and on distillation with acid ethaldehyde is obtained. Ethaldehyde is also produced on heating the pure chlorosulpho-salt with 20 times its weight of water for 24 hours at 140° (284° F.) (Bunte, *Ann. Chem. Pharm.*, clxx. 305). From this there can be little doubt that by the action of the sulphite on the dichlorethane, sodic chlorethylsulphonate is first produced:

$$CH_3.CHCl_2 + SO_3Na_2 = CH_3.CHCl.SO_3Na + NaCl,$$

and that this is then decomposed by the water and converted into sodic oxethylsulphonate and hydrochloric acid, or oxethylsulphonic acid and sodic chloride:

$$CH_3.CHCl.SO_3Na + OH_2 = CH_3.CH(OH).SO_3Na + HCl.$$

The formation of an oxethylsulphonic acid in this manner from ethaldehyde is analogous to that of the isomeric sulpho-acid, the so-called isethionic acid, from ethylenic oxide, the isomeride of ethaldehyde:



$$\left.\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\right\} O + H_2SO_3 = \begin{matrix} CH_2.OH \\ | \\ CH_2.SO_3H \end{matrix};$$

the sulpho-acid and its salts derived from ethaldehyde, like all compounds in which several negative radicles are associated with the same carbon atom, being a body of slight stability, whereas the isomeric body in which the negative radicles are associated with different carbon atoms is comparatively a very stable compound.

When ethaldehyde is dissolved in a solution of hydric ammonic sulphite, and the liquid is concentrated by evaporation over sulphuric acid, crystals are obtained of a compound which has the formula $C_2H_7NO_4S$, and therefore, contains the elements of a molecule of water less than would be the case with a body formed by the union of ethaldehyde and hydric ammonic sulphite. A substance of the same composition is obtained on passing sulphurous anhydride into an alcoholic solution of the compound of ethaldehyde and ammonia. Both crystallize in small needles, but the former requires somewhat more than six times its weight of water at 16° (60°·8 F.) to dissolve it, whilst the latter dissolves in less than one and a half parts; the former also is scarcely altered when heated at 100° (212° F.), whereas the latter rapidly loses weight and is converted into a brown resinous mass (Bunte, *loc. cit.*). Perhaps the most probable explanation of the formation of these two compounds is afforded by the following equations:

$$CH_3.COH + HSO_3NH_4 = CH_3.CH\left\{\begin{matrix}SO_3.NH_4\\OH\end{matrix}\right. = CH_3.CH\left\{\begin{matrix}SO_3\\NH_3\end{matrix}\right\} + OH_2.$$

$$CH_3.CH\left\{\begin{matrix}NH_2\\OH\end{matrix}\right. + SO_2 = CH_3.CH\left\{\begin{matrix}NH_2(SO_2)\\OH\end{matrix}\right.$$

(1630) ***Ethaldehydrol Chloracetin; Chlorethylic Acetate:*** $CH_3.CHCl(C_2H_3O_2)$. —This compound is formed by the direct union of ethaldehyde and acetic chloride, when a mixture of these two substances is heated at 100° (212° F.). It is a mobile liquid lighter than water, which slowly decomposes it, boiling at 120°—124° (248°—255°·2 F.) (Maxwell Simpson, *Compt. Rend.*, xlvii. 874). By the action of potassic acetate it is converted into *ethaldehydrol diacetin*, $CH_3.CH(C_2H_3O_2)_2$ (R. Schiff, *Deut. chem. Ges. Ber.*, ix. 304), which is also formed on heating a mixture of ethaldehyde and acetic anhydride for about twelve hours at 180° (356° F.); it boils at 169° (336°·2 F.), but appears to undergo slight decomposition (Geuther, *Ann. Chem. Pharm.*, cvi. 229).

The formation of the monochlorether, $CH_3.CHCl.OC_2H_5$, on passing hydrochloric acid gas into a solution of ethaldehyde in alcohol, and of acetal, $CH_3.CH(OC_2H_5)_2$ on heating ethaldehyde with alcohol has already been described (pp. 671, 680). The production of the former may be regarded as the result of the action of the hydrochloric acid on the compound $CH_3.CH(OH).OC_2H_5$, formed by the union of the aldehyde with the alcohol.

(1631) *Cyanethylic Alcohol:* $CH_3.CH(CN).OH$.—Anhydrous hydrocyanic acid and ethaldehyde gradually combine to form this compound when the mixture of the two substances is left at rest for ten or twelve days at 20°—30° (60°—86° F.); heating at 100° (212° F.) apparently does not facilitate their combination. It is a colourless liquid, of sharp bitter taste, miscible with water in all proportions; it is scarcely altered when heated at 150° (302° F.), but on distillation boils at about 180°—184° (356°—363°·2 F.), being partially resolved into its generators. It may also be heated with water at 150° (302° F.) for three or four hours without change; alkalies decompose it, however, with separation of ethaldehyde, and concentrated hydrochloric acid at once acts upon it at ordinary temperatures, but the two substances may be mixed at 0° (32° F.), and if the temperature of the mixture be then gradually allowed to rise it soon solidifies to a mass of crystals, the cyanide being converted into lactic acid: $CH_3.CH(OH).CN + 2OH_2 + HCl = CH_3.CH(OH).COOH + NH_4Cl$ (Simpson and Gautier, *Compt. Rend.*, lxv. 414). Lactic acid is also formed when a mixture of ethaldehyde and of solutions of hydrocyanic and hydrochloric acids is gently heated for some time.

(1632) *Trigenic Acid:* $C_4H_7N_3O_2$.—On passing the vapour of cyanic acid over ethaldehyde, violent action takes place, the liquid entering into ebullition, and carbonic anhydride being evolved; finally the whole solidifies to a mass resembling calcined borax, and on boiling this for some time with moderately strong hydrochloric acid a solution is obtained from which trigenic acid crystallizes out on cooling in small colourless prisms. It is probably formed by the displacement of one of the CO groups in the so-called cyanuric acid (1145) by the group $CH_3.CH$, and the name trigenic acid is therefore a misnomer; when ammonia and argentic nitrate are added to its aqueous solution, a colourless crystalline precipitate of the silver derivative $C_4H_6AgN_3O_2$ is thrown down.

(1633) *Action of Ammonia and of Amines on Ethaldehyde.*—On passing ammonia gas into a solution of ethaldehyde in ether, crystals are obtained of so-called aldehyde ammonia, which, however, from the manner in which it is formed and from its properties, may be regarded as *amidoethylic alcohol:* $CH_3.CH(NH_2).OH$. It crystallizes in well formed colourless rhombohedra, possessing a peculiar odour like that of mouse excrement, very soluble in water, but less soluble in alcohol and still less so in ether; it melts between 70° and 80° (158°—176° F.), and decomposes when heated higher under the ordinary atmospheric pressure, but under a low pressure it may be volatilized unchanged: thus Schroeder states that in two experiments with Hofmann's apparatus (p. 36) at 100° and 160° (212° and 320° F.) respectively, he obtained the numbers 30·33 and 30·36, the theoretical density being 30·5; at 185° (365° F.), however, the density was only 27·77, indicating that partial decomposition had taken place (*Deut. chem. Ges. Ber.*, iv. 470).

It is readily decomposed by acids, ethaldehydrol being formed, so that ethaldehyde is obtained from it on distillation with dilute acids; no ammonia is produced on treating it with alkalies in the cold. Acetic chloride and anhydride, and phosphoric pentachloride at once resolve it into ethaldehyde and ammonia, and then act upon these separately (R. Schiff).

(1634) *Compounds formed from Amidoethylic Alcohol (Aldehyde-Ammonia).*—If kept, especially when moist, the crystals of aldehyde-ammonia become yellow; this change, according to Lubavin (*Deut. chem. Ges. Ber.*, viii. 1684), is due to the action of the carbonic acid from the air. According to Strecker (*Ann. Chem. Pharm., Sup.*, vi. 255), if aldehyde-ammonia moistened with water, alcohol, or ether, be left to itself for a considerable period, it is converted into *aldehydin*, a basic substance of the composition $C_6H_{12}N_2 = 3CH_3.CH(NH_2)OH - 3OH_2 - NH_3$. Schiff has obtained the same substance by allowing a solution of ethaldehyde in an excess of a not too concentrated alcoholic solution of ammonia to stand for five or six months in a closed flask (*ibid.*, p. 1). It is an amorphous substance, very soluble in water and alcohol, forming an unstable hydrochloride with two molecules of hydrochloric acid, and a granular crystalline platinochloride of the composition $PtCl_6N_2C_6H_{14}$. When heated with water, it yields *oxytrialdin* and ammonia: $C_6H_{12}N_2 + OH_2 = NH_3 + C_6H_{11}NO$ (Schiff). This compound is also amorphous; it combines with only a single molecule of hydrochloric acid. It is not appreciably altered by heating at 150° (302° F.), but is decomposed at higher temperatures; phosphoric pentachloride only slowly acts upon it, the greater part becoming carbonized.

By heating aldehyde-ammonia with alcohol in closed vessels, still more complex substances are formed, bodies which Schiff has termed *oxytetraldin*, $C_8H_{13}NO$, and *oxypentaldin*, $C_{10}H_{15}NO$, being obtained when the temperature is maintained at about 110°—120° (230°—248° F.) for twenty-four hours; oxytetraldin is also the chief product of the decomposition of aldehyde-ammonia in open vessels at about 100° (212° F.). If the product obtained by heating aldehyde-ammonia with anhydrous alcohol at 120°—130° (248°—266° F.) for twelve hours, be distilled from the water bath until a drop of the liquid which passes over diluted with water is rendered turbid by the addition of alkali, and the residue be then distilled in a current of superheated steam, finally at a temperature of 180° (356° F.), after which it is distilled alone, an oily distillate is obtained from which a considerable quantity of *collidine*, $C_8H_{11}N$, may be separated by shaking it with hydrochloric acid, neutralizing the acid liquid with alkali, drying the oil which separates over solid potassic hydrate, and then submitting it to fractional distillation. Other basic substances of lower and higher boiling point, amongst them a body apparently polymeric with collidine, and bodies free from nitrogen are also formed (Ador and Baeyer, *Ann. Chem. Pharm.*, clv. 294). Collidine is one of several basic substances contained in the so-called Dippel's oil, obtained by distilling bones; it is also produced on heating β-dichlorethane, $CH_3.CHCl_2$, with aqueous ammonia at 160° (320° F.) (Krämer, *Deut. chem. Ges. Ber.*, iii. 262). Its formation from ethaldehyde is doubtless the end result of a series of changes, crotonic aldehyde or its ammonia compound being probably first produced; the withdrawal of the elements of a single molecule of water from the latter obviously would furnish a body of the composition of oxytetraldin, whilst if the elements of two molecules of water were split off, a body of the composition of collidine would be obtained.

Aldehyde-ammonia readily enters into reaction with a number of other substances. When it is heated with a mixture of hydrocyanic acid and dilute hydrochloric acid, *alanine* or *amidopropionic acid* is obtained; it may be supposed that in the first instance an amidocyanethane is produced:

$$CH_3.CH(NH_2)OH \ + \ HCN \ = \ CH_3.CH(NH_2)CN \ + \ OH_2,$$

which is afterwards converted into alanine:

$$CH_3.CH(NH_2)CN \ + \ 2OH_2 \ + \ HCl \ = \ CH_3.CH(NH_2)COOH \ + \ NH_4Cl.$$

But the formation of alanine would appear to be preceded by that of more complex bodies. Thus on evaporating a solution of aldehyde-ammonia in aqueous hydrocyanic acid on the water bath, a residue is obtained from which ether extracts the compound $C_9H_{15}N_5 = 3CH_3.CH(NH_2)OH + 3HCN - NH_3 - 3OH_2$. It crystallizes in long needles, which sublime undecomposed; it does not furnish a precipitate with silver solutions, and no evidence of its containing the cyanogen group is obtained on treating it with alkali and a ferrous salt; by dissolving it in hydrochloric acid and allowing the solution to evaporate spontaneously a crystalline hydrochloride is obtained (H. Strecker, *Ann. Chem. Pharm.*, cxxx. 222). If, however, aldehyde-ammonia be dissolved in hydrocyanic acid solution, and sufficient dilute hydrochloric acid be added to render the mixture distinctly acid, and it be then left to itself in a closed vessel, the liquid sooner or later becomes filled with crystals of *hydrocyanaldin*: $C_9H_{12}N_4 = 3CH_3.CH(NH_2)OH + 3HCN - 3OH_2 - 2NH_3$, especially if exposed to sunlight. This compound melts at a high temperature and sublimes unchanged if not too rapidly heated; its aqueous solution is not precipitated by silver salts, but if nitric acid be added and the liquid boiled, argentic cyanide is thrown down and an odour of ethaldehyde is apparent; on heating it with alkali, ammonia is evolved and aldehyde-resin is formed; it does not combine with acids (A. Strecker, *ibid.*, xci. 349). A third compound,

$C_4H_8N_2 = 2CH_3.CH(NH_2)OH + 2HCN - 2OH_2 - NH_3$, is obtained when a mixture of *pure* potassic cyanide and aldehyde-ammonia is decomposed by means of a spray of hydrochloric acid; it crystallizes in needles melting at 67° (152°·6 F.), and decomposes when heated higher. It is decomposed when heated with an aqueous solution of argentic nitrate in the manner represented by the equation:

$$C_4H_8N_2 + 2AgNO_3 + 2OH_2 = 2CH_3.COH + 2AgCN + NH_4NO_3 + HNO_3,$$

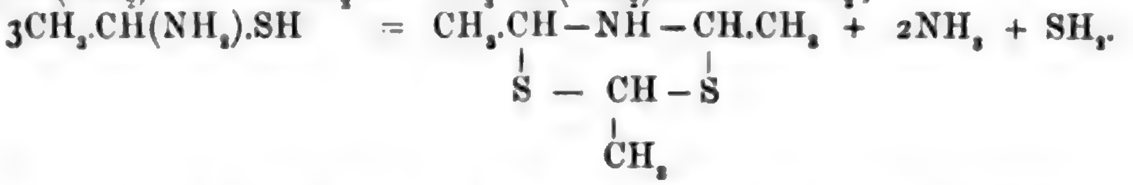
and when heated with hydrochloric acid yields ethaldehyde and alanine (Urech, *Deut. chem. Ges. Ber.*, vii. 1115).

From the properties of these different substances derived from aldehyde-ammonia, it appears highly probable that the latter is first converted into the compound $CH_3.CH(NH_2)CN$, and that even if the alanine be not directly formed from this, the more complex bodies which furnish it are produced from this cyanamido-compound by the union of several molecules and simultaneous elimination of the elements of one or more molecules of ammonia.

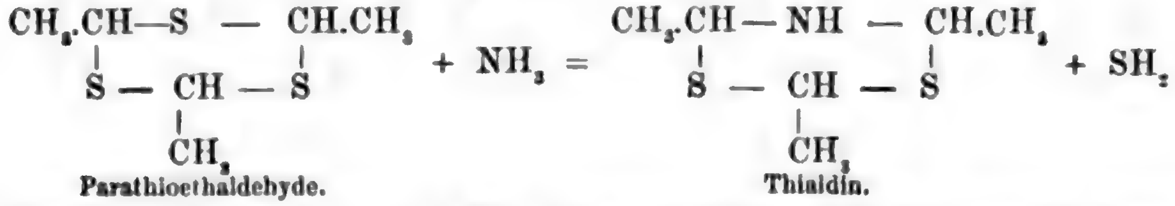
When a mixture of aldehyde-ammonia with potassic cyanide and cyanate is acted upon by acids, a crystalline body of the composition of *lactylurea*, $C_4H_6N_2O_2$, is produced, which yields alanine, carbonic anhydride, and ammonic chloride, when heated with hydrochloric acid (Urech, *loc. cit.*).

On passing sulphuretted hydrogen into an aqueous solution of aldehyde-ammonia, glistening colourless crystals of *thialdin*, $C_6H_{13}NS_2$, are obtained; the formation of this body is probably preceded by that of the thio-compound corresponding to aldehyde-ammonia, thus:

$$CH_3.CH(NH_2).OH + SH_2 = CH_3.CH(NH_2).SH + OH_2;$$



Thialdin may also be prepared by the action of ammonia on parathioethaldehyde, its formation from which may be regarded as the result of the displacement of one of the atoms of sulphur by the group (NH)″:



Parathioethaldehyde. Thialdin.

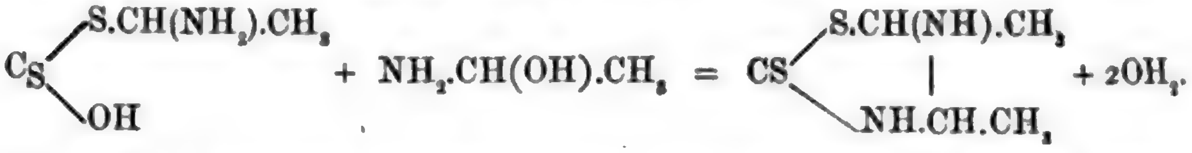
Thialdin melts at 43° (109°·4 F.); it may be distilled with the vapour of water, and sublimes unchanged at ordinary temperatures, but decomposes when distilled alone. It dissolves readily in acids, and forms crystalline salts such as the hydrochloride $C_6H_{14}NS_2Cl$; it also exhibits the behaviour of a tertiary amine in combining with the moniodoparaffins. It furnishes precipitates with a number of metallic salts, which, however, rapidly decompose, metallic sulphide being formed; it is decomposed when warmed with a solution of argentic nitrate, ethaldehyde, ammonic nitrate, and argentic sulphide being produced.

A corresponding *selenaldin*, $C_6H_{13}NSe_2$, is obtained by the action of seleniuretted hydrogen on aldehyde-ammonia.

On adding carbonic bisulphide to an alcoholic solution of aldehyde-ammonia, the alkaline reaction at once disappears, the temperature rises, and in a few minutes white glistening crystals of *carbothialdin*, $C_5H_{10}N_2S_2$, separate from the solution. Perhaps the bisulphide unites in the first instance with the amido-ethylic alcohol to form a thiocarbonate, thus:

$$CH_3.CH\left\{\begin{matrix}OH\\NH_2\end{matrix}\right. + CS_2 = CS\left\}\begin{matrix}OH\\S.CH(NH_2).CH_3,\end{matrix}\right.$$

which then enters into reaction with a second molecule of the amido-compound:



Carbothialdin is almost insoluble in water, but dissolves readily in hot alcohol. It is immediately dissolved by dilute hydrochloric acid, and is reprecipitated unchanged if ammonia be then added, but if the solution be allowed to stand it coagulates in consequence of the separation of a yellowish white insoluble substance; on boiling it with an excess of acid, it is resolved into ethaldehyde, carbonic bisulphide, and an ammonic salt. It furnishes precipitates with a number of metallic salts, which readily decompose on standing.

The behaviour of ethaldehyde with the amines derived from the paraffins does not appear to have been investigated. When aniline and ethaldehyde are mixed, a violent reaction takes place, a thick brown liquid and water being formed; if the two substances are previously cooled in a mixture of ice and salt, and then mixed, the reaction also takes place at once, but the product is only yellow. To complete the reaction, the mass is heated at 100° (212° F.) for a few hours. The product then consists of a mixture of two compounds formed by the action of one and two molecules respectively of ethaldehyde on two molecules of aniline, $NH_2.C_6H_5$, and which are represented by the formulæ:

$$CH_3.CH\left\{\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. \qquad CH_3.CH\left\{\begin{matrix}N.C_6H_5\\N.C_6H_5\end{matrix}\right\}CH.CH_3.$$

They may be separated by means of boiling alcohol, in which the former is sparingly but the latter readily soluble; only the former has been obtained in crystals (Schiff, *Ann. Chem. Pharm., Sup.*, iii. 344).

(1635) *Action of Ethaldehyde on Acid Amides.*—By heating ethaldehyde with acetamide, $CH_3.CO(NH_2)$, in sealed tubes, it is readily converted into the compound $CH_3.CH(NH.CO.CH_3)_2$; this body crystallizes in large prisms, which melt at 169° (336°·2 F.); acids decompose it with formation of ethaldehyde (Tawildarow, *Deut. chem. Ges. Ber.*, v. 477).

Benzamide yields a similar compound: although this amide is not soluble in pure ethaldehyde, it readily dissolves on the addition of a few drops of dilute hydrochloric acid, heat being developed; on cooling, the solution solidifies to a white crystalline mass of *ethylidenedibenzamide*, $CH_3.CH(NH.CO.C_6H_5)_2$. It melts at 188° (370°·4 F.); when heated with dilute acids, it is readily converted into ethaldehyde and benzamide (Nencki, *ibid.*, vii. 158). The same compound is formed when cyanobenzene (benzonitrile) is added to a solution of parethaldehyde in sulphuric acid, and other cyanides yield analogous products (Hepp and Spiess, *ibid.*, ix. 1424).

Ethylic carbonate (urethane), $NH_2.CO.OC_2H_5$, behaves in a precisely similar manner, the formation of the compound $CH_3.CH(NH.CO.OC_2H_5)_2$ taking place at once on the addition of a few drops of hydrochloric acid to the solution of urethane in ethaldehyde. It melts at 126° (258°·8 F.), and is readily decomposed by acids (Nencki). The same compound is formed when a mixture of acetal, $CH_3.CH(OC_2H_5)_2$, and urethane with concentrated hydrochloric acid is allowed to stand (Bischoff, *ibid.*, vii. 629).

By passing chlorine into alcohol saturated with the vapour of hydrocyanic acid, or a solution of mercuric cyanide in alcohol, Stenhouse obtained a crystalline compound of the formula $C_8H_{14}Cl_2N_2O_4$. On repeating these experiments, Bischoff (*ibid.*, v. 80) also obtained this compound, but found that sometimes a corresponding monochlorinated compound, $C_8H_{15}ClN_2O_4$, was formed, the latter being more frequently produced when a solution of mercuric cyanide was employed; and afterwards he succeeded in obtaining this monochlorinated compound by the action of monochloracetal on urethane in presence of hydrochloric acid. Hence there can be no doubt that the bodies thus obtained are chlorinated derivatives of ethylideneurethane, mono- and dichloracetal may both be produced by the action of chlorine on alcohol (p. 681), and as hydrocyanic acid yields cyanogen chloride when acted upon by chlorine, and cyanogen chloride and alcohol yield urethane; the formation of bodies derived from urethane and mono- and dichloracetal by the action of chlorine on a mixture of hydrocyanic acid and alcohol is therefore readily understood.

Urea, $CO(NH_2)_2$, readily dissolves in a mixture of ethaldehyde with an equal volume of alcohol, its solution being attended with development of heat. After a few hours the solution begins to deposit crystals, and finally the whole solidifies to a mass of aggregates of small needles of *ethylideneurea*, $CH_3.CH\left\{\begin{matrix}NH\\NH\end{matrix}\right\}CO$. The same compound is obtained if an aqueous solution of ethaldehyde be employed. Moderately concentrated acids at once reconvert ethylideneurea into ethaldehyde and urea; it appears to be destitute of basic properties (Schiff, *Ann. Chem. Pharm.*, cli. 206). A corresponding compound is formed on heating thiourea, $CS(NH_2)_2$, with ethaldehyde in sealed tubes at 100° (212° F.) (Reynolds, *Deut. chem. Ges. Ber.*, iv. 806).

If a moderately concentrated solution of aldehyde-ammonia and thiourea be heated in an open dish, as soon as it begins to boil it solidifies to a mass of crystals of the composition $C_5H_{11}N_3S$ (Nencki, *ibid.*, vii. 162). On boiling the aqueous solution of this compound, it is gradually decomposed into ammonia, thiourea, and ethaldehyde; its formation probably takes place in the following manner:

$$2NH_2.CH(CH_3).OH + CS(NH_2)_2 = \left.\begin{matrix}NH_2.CH(CH_3).HN\\NH_2.CH(CH_3).HN\end{matrix}\right\}CS + 2OH_2;$$

$$\left.\begin{matrix}NH_2.CH(CH_3).HN\\NH_2.CH(CH_3).HN\end{matrix}\right\}CS = NH_3 + NH\left\{\begin{matrix}CH(CH_3).HN\\CH(CH_3).HN\end{matrix}\right\}CS.$$

When cyanogen gas is passed into crude ethaldehyde, a white pulverulent precipitate of the composition $C_6H_{10}N_4O_4$ is obtained (Berthelot and Saint Gilles, *Compt. Rend.*, lvi. 1171). This body is doubtless derived from oxamide, which is the first product of the action of water on cyanogen, and may be represented by the formula, $CH_3.CH(NH.CO.CO.NH_2)_2$. Its formation in this manner explains Liebig's observation that when a small quantity of ethaldehyde is added to a solution of cyanogen, the latter remains colourless, gradually depositing oxamide, into which the whole of the cyanogen ultimately undergoes conversion; whereas without the aldehyde the solution rapidly becomes brown, and the cyanogen is converted into ammonic oxalate, urea, &c. In presence of the aldehyde the cyanogen is probably converted into ethylideneoxamide, which is gradually decomposed by the water into ethaldehyde and oxamide; and the aldehyde thus liberated again forms ethylideneoxamide, which is again decomposed, so that a small quantity of aldehyde suffices to effect the conversion of a large amount of cyanogen into oxamide.

The isothiocyanates also enter into reaction with aldehyde-ammonia (R. Schiff, *Deut. chem. Ges. Ber.*, ix. 565).

(1636) *Action of Aldehyde on Hydrocarbons.*—Concentrated sulphuric acid at once decomposes ethaldehyde, so that products of its action on benzene are not obtained on mixing it with a solution of this hydrocarbon in sulphuric acid, but if the more stable parethaldehyde be carefully dissolved in the acid, and benzene be then added to the solution, the hydrocarbon *diphenylethane* is produced:

$$CH_3.COH + 2C_6H_6 = CH_3.CH(C_6H_5)_2 + OH_2.$$

Condensation products are also formed by the action of aldehyde on phenol and pyrogallol in presence of hydrochloric or sulphuric acid (Baeyer, *Deut. chem. Ges. Ber.*, vii. 1190).

(1637) PARATHIOETHALDEHYDE.—On passing sulphuretted hydrogen into an aqueous solution of ethaldehyde, the liquid becomes turbid, and when saturated deposits a viscid oil of most unpleasant odour. Weidenbusch regarded this as a compound of thioethaldehyde and sulphuretted hydrogen, but Pinner came to the conclusion that it was a compound of ethaldehyde and thioethaldehyde of the formula $C_2H_4O.C_2H_4S$ (*Deut. chem. Ges. Ber.*, iv. 257). When treated with acids, it solidifies to a crystalline mass of parathioethaldehyde, $C_6H_{12}S_3$; it has recently been stated by Klinger (*ibid.*, ix. 1893) that the amount of parathioaldehyde thus obtained is nearly equal to the amount of oil acted upon, and he therefore concludes that the oil is really thioethaldehyde, mixed perhaps with a small quantity of the compound $CH_3.CH(OH).SH$, which doubtless is the first product of the action of sulphuretted hydrogen on ethaldehydrol (comp. p. 719).

If sulphuretted hydrogen is passed into an acid solution of ethaldehyde, the solid parathioaldehyde at once separates. It crystallizes in brilliant white glistening needles, soluble in alcohol and ether; it begins to sublime at 45° (113° F.), and may be volatilized unchanged, its vapour density corresponding with the formula $C_6H_{12}S_3$ (Hofmann, *ibid.*, iii. 588). It forms a crystalline compound with argentic nitrate, $C_6H_{12}S_3.2AgNO_3$, which is obtained on adding argentic nitrate to its solution in alcohol. When parathioethaldehyde is warmed on the water bath with acetic or benzoic chloride, a violent reaction takes place, and it is converted into a body of the same empirical composition, but which crystallizes from acetic acid in long glistening needles, melting at 125° (257° F.), and boiling at 145°—150° (293°—302° F.) almost without change. This modification of thioethaldehyde forms two crystalline compounds with argentic nitrate of the empirical composition $C_6H_{12}S_3.AgNO_3$, and $C_6H_{12}S_3.3AgNO_3$ (Klinger, *loc. cit.*).

(1638) HALOID DERIVATIVES OF ETHALDEHYDE—CHLORETHALDEHYDE.—According to Glinsky, when gaseous monochlorethylene, C_2H_3Cl, is passed into a well-cooled aqueous solution of hypochlorous acid in which mercuric oxide is suspended, it is readily absorbed, much heat being developed; if the solution be preserved in a stoppered flask, a crystalline crust forms at the bottom of the vessel, consisting of a compound of chloraldehyde with mercurous chloride, $C_2H_3ClO.Hg_2Cl_2$. If, however, the liquid be distilled, a distillate containing the hydrate of monochloraldehyde is obtained. This hydrate is said to crystallize from ether in flat plates of the composition $2C_2H_3ClO.OH_2$, which melt at about 75° (167° F.). It reduces an ammoniacal solution of a silver salt, and oxidizes on exposure to the air, forming chloracetic acid. Sulphuric acid converts it into a thick brownish-yellow oil. It unites with hydric sodic sulphite, forming the compound $(C_2H_3ClO.HNaSO_3)_2.OH_2$, which separates from boiling alcohol as a bulky white crystalline powder. On boiling its solution with potassic iodide, iodaldehyde is produced. On treatment with potassic cyanide it forms an oil which is converted by the action of hydrochloric acid into chlorolactic acid (*Zeits. Chem.* [2], iii. 676; iv. 617; vi. 513, 647).

These statements with regard to chloraldehyde require revision. Probably the so-called hydrate is a body of the composition $(CH_2Cl.CH.OH)_2O$, formed by the action of water on the compound $CH_2Cl.CHCl.OH$, which is perhaps the first product of the action of hypochlorous acid on monochlorethylene, thus:

$$CH_2{=}CHCl + ClOH = CH_2Cl.CHCl.OH;$$
$$2CH_2Cl.CHCl.OH + OH_2 = (CH_2Cl.CH.OH)_2O + 2HCl.$$

Chloraldehyde would doubtless be obtained on treating monochloracetal, which according to Bischoff may be produced by the action of chlorine on acetal (*Deut. chem. Ges. Ber.*, vii. 630), with sulphuric acid. According to Jacobsen and Abeljanz, monochloraldehyde is a product of the action of sulphuric acid and of water on dichlorether (p. 672), but it has not been isolated. Hepp (*Deut. chem. Ges. Ber.*, vii. 1409) has obtained a number of chlorinated hydrocarbons by the action of this aldehyde—*i.e.*, of the solution of dichlorether in sulphuric acid, on benzene and its homologues.

DICHLORETHALDEHYDE: $CHCl_2.COH$, is obtained by distilling a mixture of dichloracetal (p. 681) with 4—6 vols. of sulphuric acid from an oil bath at about 130° (266° F.). It is a colourless mobile liquid, boiling at 88°—90° (190°·4—194° F.). Dichlorethaldehyde is readily converted into dichloracetic acid by oxidation with nitric acid, but little alteration takes place on passing its vapour mixed with air over heated spongy platinum. When poured into water it first sinks to the bottom and then dissolves, forming the aldehydrol (p. 514) (Paterno), which is also one of the products of the action of chlorine on a solution of ethaldehyde in water or hydrochloric acid (Wurtz). When left to itself, it changes into a white, amorphous, insoluble polymeride, which may be depolymerized by heating at 120° (248° F.). This polymeride alone is formed when dichlorethaldehyde is mixed with a small quantity of hydrochloric acid, but if dichlorethaldehyde be left in contact with sulphuric acid, it is converted into a crystalline polymeride easily soluble in hot alcohol, but almost insoluble in water. It melts at 130° (266° F.); if heated in a closed tube at 245°—250° (473°—482° F.), it is readily reconverted into the liquid modification, this change taking place at 120°—130° (248°—266° F.) in presence of concentrated sulphuric acid (Jacobsen, *Deut. chem. Ges. Ber.*, viii. 87).

TRICHLORETHALDEHYDE or *Chloral*: $CCl_3.COH$.—This compound is most readily obtained by agitating the mixture of trichlethaldehydrol, $CCl_3.CH(OH)_2$, and of its monethylin, $CCl_3.CH(OH).OC_2H_5$, formed on saturating anhydrous alcohol with chlorine gas (comp. p. 429), with about four times its volume of sulphuric acid, and then rectifying the oily layer which separates. It may be prepared in a similar manner by heating trichloracetal (p. 681) with sulphuric acid at 150° (302° F.). All substances which furnish ethaldehyde on oxidation furnish trichlorethaldehydrol on distillation with hydrochloric acid and manganic peroxide; hence chloral may be obtained from bodies such as sugar and starch.

Chloral is a colourless mobile liquid, of peculiar pungent odour; its vapour exercises a very irritating action on the eyes, and the liquid acts strongly on the skin. It boils at 94°·5 (202°·1 F.), and at 18° (64°·4 F.) has the sp. gr. 1·502. It readily undergoes conversion into a white amorphous polymeride (*metachloral*), which distils at about 180° (356 F.), being reconverted into liquid chloral; this change apparently requires the presence of a foreign substance, but is effected by very minute quantities of the polymerizing agent (comp. Grabowski, *Deut. chem. Ges. Ber.*, viii. 1437). Metachloral is insoluble in and unaffected by water, alcohol, and ether.

Chloral is reconverted into ethaldehyde by the action of the nascent hydrogen furnished by a mixture of zinc and hydrochloric acid. It does not absorb oxygen on exposure to the air, but is converted into trichloracetic acid, $CCl_3.COOH$, by the action of oxidizing agents, such as concentrated nitric acid, potassic permanganate, &c. It readily combines with water, forming crystalline trichlorethaldehydrol or chloralhydrate, $CCl_3.CH(OH)_2$ (p. 513), much heat being developed in the reaction. In a similar manner, it forms compounds with ethylic alcohol and its homologues and other carbinols, and with thioethylic alcohol (comp. 1601), glycol, glycerol, ethylic lactate and tartrate, and indeed with hydroxyl compounds generally (Henry, *ibid.*, vii. 762). It also unites with acetic chloride and acetic anhydride, forming the compounds $CCl_3.CHCl(C_2H_3O_2)$ and $CCl_3.CH(C_2H_3O_2)_2$ (Meyer and Dulk, *Ann. Chem. Pharm.*, clxxi. 65). Alkalies convert it into trichloromethane or chloroform, and a formate: $CCl_3COH + KHO = CCl_3H + HCOOK$. When distilled with phosphoric pentachloride it yields pentachlorethane, $CHCl_2.CCl_3$; similarly, the chlorobromide PCl_3Br_2 converts it into *dibromotrichlorethane*, $CCl_3.CHBr_2$, which boils at about 200° (392° F.) with partial decomposition (Paterno).

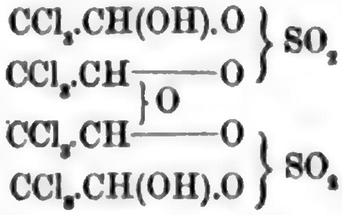
When chloral is digested with a concentrated aqueous solution of hydrocyanic acid, it is converted into the hydrocyanide, $CCl_3.CH(OH).CN$, which on digestion with moderately concentrated hydrochloric acid yields *trichlorolactic* acid, $CCl_3.CH(OH).COOH$ (Bischoff and Pinner, *Ann. Chem. Pharm.*, clxxix. 741). This cyanide is probably formed from the aldehydrol in the following manner:

$$CCl_3.CH(OH)_2 \ + \ HCN \ = \ CCl_3.CH(OH).CN \ + \ OH_2,$$

for it is not produced when chloral and hydrocyanic acid alone are digested together. It crystallizes in rhombic prisms, which melt at about 61° (141°·8 F.). It combines directly with cyanic acid, forming a crystalline compound of the formula $C_4Cl_3H_3N_2O_3$ (Cech, *Deut. chem. Ges. Ber.*, viii. 1174).

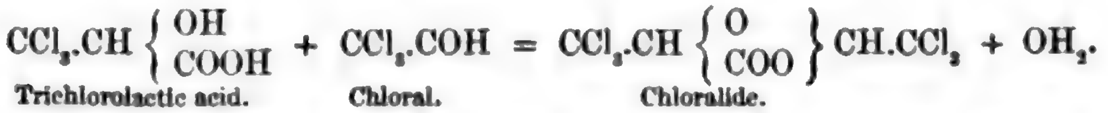
Concentrated sulphuric acid is without immediate action on chloral, but after a time converts it into metachloral. If, however, chloral (? chloral-hydrate) be mixed with fuming sulphuric acid, the mixture solidifies after some time to a crystalline mass of the composition $C_8H_6Cl_{12}S_2O_{11}$; whilst if the vapour of sulphuric anhydride be passed into chloral (? chloral-hydrate), a body of the composition $C_{10}H_9Cl_{15}S_2O_{14}$ is obtained (Grabowski, *Deut. chem. Ges. Ber.*, vi. 225, 1070). Both are decomposed by hot water, with formation of sulphuric acid and chloral-hydrate; if carefully warmed with alcohol, however, the latter dissolves unchanged, crystallizing out on cooling in needles which melt at 70° (158° F.). Grabowski has also described two other compounds of a similar kind. The relation of the first of the compounds described to chloral-hydrate may be represented by the following formula:

$$CCl_3.CH(OH)_2$$



$$\begin{array}{l} \left.\begin{array}{l} CCl_3.CH(OH).O \\ CCl_3.CH\text{——}O \end{array}\right\} SO_2 \\ \quad\quad\quad \Big\} O \\ \left.\begin{array}{l} CCl_3.CH\text{——}O \\ CCl_3.CH(OH).O \end{array}\right\} SO_2 \end{array}$$

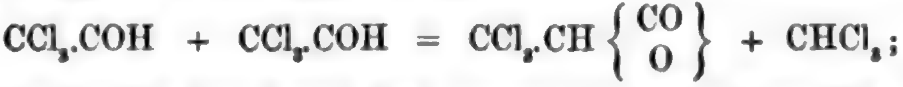
If the mixture of chloral and pyrosulphuric acid be heated for some time, so-called *chloralide*, $C_6H_2Cl_6O_3$, is obtained. The best method of preparing this body is to heat a mixture of 1 part fuming sulphuric acid and 3 parts chloral in a retort with reversed condenser until the temperature of the mixture reaches 105° (221° F.) (Grabowski, *ibid.*, viii. 1433). It crystallizes from boiling alcohol in long prisms, possessing a faint peculiar odour, which melt at about 115° (239° F.); it boils at 268° (514°·4 F.), or, according to Wallach, at 272° (521°·6 F.), without undergoing the least decomposition. The formation of chloralide affords an extremely interesting example of condensation. Wallach found (*ibid.*, viii. 1578) that when it was treated with zinc and hydrochloric acid in alcoholic solution, ethaldehyde and dichloracrylic acid, $C_3H_2Cl_2O_2$, were produced; and that if it were heated in sealed tubes with alcohol it was converted into chloral alcoholate and *ethylic trichlorolactate*, $CCl_3.CH(OH).COOC_2H_5$, the latter compound being identical with the ethylic salt of the trichlorolactic acid obtained from chloral as described on p. 744. He was thus led to regard it as formed from trichlorolactic acid and chloral in the manner represented by the following equation, and succeeded in preparing it by heating a mixture of these substances at 150°—160° (302°—320° F.) (*ibid.*, ix. 545):



$$CCl_3.CH\left\{\begin{matrix}OH\\COOH\end{matrix}\right. + CCl_3.COH = CCl_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.CCl_3 + OH_2.$$

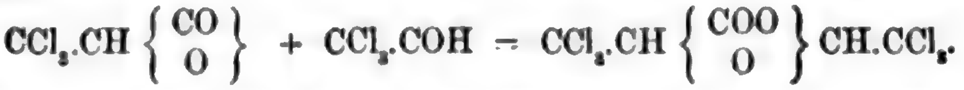
Trichlorolactic acid. Chloral. Chloralide.

In its formation from chloral, the latter is probably first converted into chlorolactide, although it is difficult to say in what manner the change takes place, and what part is played by the sulphuric acid:



$$CCl_3.COH + CCl_3.COH = CCl_3.CH\left\{\begin{matrix}CO\\O\end{matrix}\right\} + CHCl_3;$$

and the chlorolactide thus formed then enters into combination with a molecule of chloral:



$$CCl_3.CH\left\{\begin{matrix}CO\\O\end{matrix}\right\} + CCl_3.COH = CCl_3.CH\left\{\begin{matrix}COO\\O\end{matrix}\right\}CH.CCl_3.$$

The trichloromethane, which is the accessory product, is decomposed by the sulphuric acid in the following manner:

$$CHCl_3 + H_2S_2O_7 = CO + HCl + 2SO_2HCl.$$

Chloral forms crystalline compounds with acid sulphites. When cold concentrated solutions of chloral-hydrate and of potassic sulphite are mixed, the liquid soon solidifies to a mass of glistening crystalline plates of the compound $CCl_3.CH(OH).KSO_3$, and at the same time trichloromethane is produced:

$$2CCl_3.CH(OH)_2 + K_2SO_3 = CCl_3.CH(OH).SO_3K + H.COOK + CHCl_3 + OH_2.$$

If the solution be heated, other products formed by the displacement of the chlorine in the compound $CCl_3.CH(OH).SO_3K$ are obtained—viz., a difficultly soluble salt of the composition $CH(SO_3K)_2.CH(OH).SO_3K + OH_2$, and a very soluble double salt: $CCl(SO_3K)_2.CH(OH).SO_3K + 2CHCl(SO_3K).CH(OH).SO_3K + 7OH_2$. The former salt is decomposed when boiled with potassic carbonate solution, its behaviour being similar to that of chloral-hydrate itself:

$$CH(SO_3K)_2.CH(OH).SO_3K + K_2CO_3 = CH_2(SO_3K)_2 + K_2SO_3 + HCOOK + CO_2.$$

By the action of bromine, or of hydrochloric acid, it is converted into potassic aldehydodisulphonate, $CH(SO_3K)_2.COH$, which readily combines with the acid sulphite to form the parent salt; when digested with bromine, it yields the bromo-derivative, $CBr(SO_3K)_2.COH$, which on mere boiling for a few seconds with potassic sulphite yields the original salt, $CH(SO_3K)_2.CH(OH).SO_3K$. Pungent-smelling volatile products are also formed on heating chloral-hydrate with potassic sulphite, so that probably a portion of the former is reduced to mono- or dichloraldehyde hydrate (Rathke, *Ann. Chem. Pharm.*, clxi. 149).

Chloral forms a crystalline compound with ammonia, $CCl_3.CH(OH).NH_2$; this body is obtained on passing ammonia into well cooled chloral, much heat being developed in the reaction, so that unless very small quantities are operated upon, secondary products are also formed; but it is much more readily produced by passing a rapid current of ammonia gas into a well cooled solution of chloral in chloroform until the whole suddenly solidifies (R. Schiff, *Deut. chem. Ges. Ber.*, x. 65). On treatment with concentrated sulphuric acid, it yields chloral and ammonic sulphate; and on distillation is split up into formamide, $HCO.NH_2$, and trichloromethane. By the action of acetic chloride at the ordinary temperature, it is converted into the compound $CCl_3.CH(OH).NH(C_2H_3O)$, which, on heating with acetic chloride at 120° (248° F.), yields the compound $CCl_3.CH(C_2H_3O_2).NH(C_2H_3O)$ (R. Schiff). The primary amines derived from the paraffins behave like ammonia, combining directly with chloral, and yielding compounds which are split up on distillation into trichloromethane and a formamide. Thus, with ethylamine, it forms a white crystalline compound, $CCl_3.CH(OH).NH(C_2H_5)$, which on distillation yields *formethylamide*, $HCO.NH(C_2H_5)$; similarly, ethylenediamine and chloral act energetically upon each other, forming trichloromethane and *diformylethylenediamide*:

$$(C_2H_4)H_4N_2 + 2CCl_3.COH = (HCO)_2N_2H_2(C_2H_4) + 2CHCl_3,$$

the compound first formed being at once decomposed (Hofmann, *Deut. chem. Ges. Ber.*, v. 247). The primary amines derived from the hydrocarbons of the benzene series behave somewhat differently, acting on chloral as on ethaldehyde. Thus with aniline it enters into reaction in the following manner:

$$CCl_3.COH + 2NH_2.C_6H_5 = CCl_3.CH(NH.C_6H_5)_2 + OH_2.$$

The product is a crystalline substance, which is very readily decomposed, aniline hydrochloride being at once separated on passing hydrochloric acid gas into its solution in benzene. It does not appear to possess basic properties. Paratoluidine, $NH_2.C_6H_4.CH_3$, like aniline, readily enters into reaction with chloral, much heat being developed, and forms a corresponding compound, $CCl_3.CH(NH.C_6H_4.CH_3)_2$; if alcohol be added immediately to the product of the reaction, or even if it be several times recrystallized from alcohol, it is partially converted into the compound $CCl_3.CH\left\{\begin{array}{l}OC_2H_5\\NH.C_6H_4(CH_3),\end{array}\right.$ which is remarkable for the facility with which it crystallizes. This body is always formed when a mixture of alcoholic solutions of chloral and paratoluidine is maintained for several days at a gentle heat, but corresponding compounds could not be obtained with methylic alcohol, or aniline, or xylidine, although the last-mentioned substance is acted upon by chloral in the same manner as aniline (Wallach, *Ann. Chem. Pharm.*, clxxiii. 274).

Acid amides act towards chloral like ammonia, combining directly with it; with acetamide, $NH_2.CO(CH_3)$, for example, it forms the compound $CCl_3.CH(OH).NH.CO(CH_3)$, which is also obtained as above stated on treating the compound of chloral and ammonia with acetic chloride. Benzamide and urea furnish similar compounds, the latter combining with one and two molecules of chloral forming bodies which may be represented by the formulæ:

$$CCl_3.CH(OH).(NH.CO.NH_2) \text{ and } CO(NH)_2.(CCl_3.CH.OH)_2$$

(Jacobsen, *ibid.*, clvii. 245; Wallach, *loc. cit.*). In presence of hydrochloric or sulphuric acid, chloral and ethylic carbonate (urethane), $NH_2.CO.OC_2H_5$, combine to form $CCl_3.CH(OH).NH.COOC_2H_5$ (Bischoff).

When chloral is brought into contact with trimethylamine, a vigorous reaction takes place, and a brilliant white solid substance is produced, entirely free from nitrogen. It apparently is a mixture of several substances—probably of polymerides of chloral—as it is only partially dissolved on treatment with various solvents (Meyer and Dulk, *ibid.*, clxxi. 76).

On passing the vapour of cyanic acid into chloral, it is absorbed without much heat being developed; the saturated solution sometimes solidifies immediately, but at other times only on standing, gas being also in some cases evolved, forming a vitreous mass, which on boiling with moderately concentrated hydrochloric acid is converted into a granular powder, insoluble in water, but soluble in alcohol and ether. The compound thus produced has the composition $C_5H_3Cl_6NO_3$, being formed of the elements of a molecule of cyanic acid and of two molecules of chloral (Bischoff, *Deut. chem. Ges. Ber.*, v. 86).

When chloral is mixed with concentrated sulphuric acid and benzene, it enters into reaction with the latter, forming the chlorinated hydrocarbon $CCl_3.CH(C_6H_5)_2 = CCl_3.COH + 2C_6H_6 - OH_2$. The homologues of benzene and other hydrocarbons in which the carbon atoms are united in a closed chain behave with chloral in a precisely similar manner; a number of the products so obtained have already been described under hydrocarbons. The phenols also furnish analogous products, thymol yielding the compound $CCl_3.CH(C_{10}H_{12}.OH)_2$ (Jæger, *ibid.*, vii. 1197).

From the foregoing description of trichlorethaldehyde, it will be evident that it manifests a close resemblance to ethaldehyde in many of its properties, the chief difference being that it far more readily enters into combination with other substances, and that it manifests a tendency to unite directly with substances which act upon it rather than to form condensation products by the separation of its oxygen in combination with hydrogen of the reacting body—a class of reaction which is especially characteristic of ethaldehyde.

Dibromethaldehyde: $CHBr_2.COH$.—This compound may be prepared by distilling the product of the action of two mols. bromine on a solution of one mol. ethaldehyde in twice its bulk of ethylic acetate, and agitating the portion which passes over between 120°—150° (248°—302° F.) with 3—4 vols. of concentrated sulphuric acid; the oil separated from the acid is then submitted to fractional distillation. It is a heavy oily liquid, very easily soluble in water and alcohol, with which it combines; it boils at about 142° (287°·6 F.). When kept, it undergoes conversion into a white solid insoluble polymeride. It is readily decomposed by alkalies, but does not furnish dibromomethane.

Tribromethaldehyde or *Bromal:* $CBr_3.COH$, may be prepared in a similar manner, or, like chloral, from the product of the action of an excess of bromine on anhydrous alcohol. It is a colourless heavy oil, of peculiar pungent odour, boiling at 173° (343°·4 F.); it appears to behave in every respect like trichlorethaldehyde.

(1639) HIGHER HOMOLOGUES OF ETHALDEHYDE.—In their general properties the higher homologues appear to closely resemble ethaldehyde; but as the series is ascended they become less and less soluble in water; and the same is true of most of their derivatives, as compared with those of ethaldehyde. Most noteworthy, however, is the fact that the tendency to combine with other bodies, and the stability of the resulting compounds, diminishes as the series is ascended.

(1640) PROPALDEHYDE; PROPIONIC OR PROPYLIC ALDEHYDE: $C_3H_6O = CH_3.CH_2.COH$.—This aldehyde has been prepared by the oxidation of propylic alcohol, and by distillation of a mixture of calcic propionate and calcic formate; it is produced together with acetone on heating β-dichloropropane, $CH_3.CHCl.CH_2Cl$, with water at 210°—220° (410°—428° F.), although β-di*bromo*propane yields only acetone when thus treated (Linnemann, *Ann. Chem. Pharm.*, clxi. 64).

In odour and appearance, propaldehyde closely resembles ethaldehyde, but requires five times its volume of water at 20° (68° F.) to dissolve it; according to Linnemann (*loc. cit.*, p. 22) its corrected boiling point is 48°·8 (119°·8 F.), but according to Rossi (*ibid.*, clix. 79) it boils at 49°·5 (121°·1 F.) under the pressure of 740 mm. of mercury; it has the sp. gr. ·8074 at 21° (69°·8 F.). Propaldehyde readily oxidizes on exposure to the air; it dissolves in a concentrated solution of sodic hydric sulphite with considerable development of heat, the resulting compound remaining in solution: it is very readily altered by potassic hydrate.

(1641) TETRALDEHYDES: $C_3H_7.COH$—*Normal Tetraldehyde; Butyric* or *Butylic Aldehyde:* $CH_3.CH_2.CH_2.COH$.—This aldehyde has been obtained by distillation of a mixture of calcic butyrate and calcic formate, but has not yet been prepared in a pure state. It possesses the peculiar penetrating odour which characterizes its lower homologues, and boils at about 75° (167° F.); it requires about 27 parts of water to dissolve it (Lieben and Rossi, *ibid.*, clviii. 148).

(1642) *Tetraldol; Oxybutyric Aldehyde* or *Aldol:** $CH_3.CH(OH).CH_2.COH$.—The formation of this compound from ethaldehyde has already been discussed (pp. 717—719). To prepare it, one part of ethaldehyde is mixed with one part of water and two parts of hydrochloric acid, and the mixture is left to itself for several days at a temperature of 15°—20° (59°—68° F.). As soon as it has acquired a tawny colour, and smells but slightly of ethaldehyde, it is neutralized with solid sodic carbonate, and agitated several times with ether; the ether is then distilled off from the extract, and the residue distilled under reduced pressure. At first ether and water pass over, and afterwards, between 90° and 105° (194°—221° F.), under a pressure of 20 mm., the tetraldol distils over as a colourless limpid liquid. It is miscible with water and alcohol in all proportions; when heated above 100° (212° F.) under the ordinary pressure, it begins to decompose at about 135° (275° F.) into water and crotonic aldehyde, $C_4H_8O_2 = C_4H_6O + OH_2$. It is a powerful reducing agent, precipitating cuprous oxide from an alkaline solution of a cupric salt, and metallic silver from an ammoniacal solution of argentic nitrate; it is violently oxidized by nitric and chromic acids, and on treatment with argentic hydrate is converted into the silver salt of the so-called β-oxybutyric acid, $CH_3.CH(OH).CH_2.COOH$. When submitted to the action of nascent hydrogen, it yields the glycol $CH_3.CH(OH).CH_2.CH_2.OH$. It combines with ammonia, forming a compound which, on decomposition by heat, yields collidine or an isomeric body and other basic products.

Tetraldol rapidly undergoes polymerization. Although perfectly limpid when freshly distilled, it soon becomes viscid, the change being attended with development of heat, and if allowed to stand for some weeks, crystals separate. This crystalline polymeride is also easily soluble in water and alcohol; it begins to soften at 80° (176° F.), and distils in vacuo between 90° and 100° (194°—212° F.), being reconverted into the liquid modification.

If the liquid obtained by heating ethaldehyde with water and hydrochloric acid as above described be allowed to stand until it acquires a brown tint and opaline appearance, and be then neutralized and treated with ether, &c., a crystalline product is obtained which is apparently formed from tetraldol in precisely the same manner that crotonic aldehyde is formed from ethaldehyde:

$$\underset{\text{Ethaldehyde.}}{2CH_3.COH} = \underset{\text{Crotonic aldehyde.}}{CH_3.CH{=}CH.COH} + OH_2.$$

$$2CH_3.CH(OH).CH_2.COH = CH_3.CH(OH).CH_2.CH{=}CH.CH(OH).CH_2.COH + OH_2.$$

The "aldol" thus produced is soluble in boiling water, but crystallizes out in great part on cooling in brilliant scales; it melts at 139° (282°·2 F.), and distils at 139° (278°·6 F.) under a pressure of 20 mm. of mercury. By digestion with argentic hydrate it is converted into the corresponding monobasic acid, $C_8H_{14}O_4$.

Tetraldol also loses water when heated for several hours at 60° (140° F.) in a current of dry air; it then thickens, and solidifies on cooling to a colourless, transparent, viscid mass, insoluble in water (Wurtz, *Compt. Rend.*, lxxiv. 1361; lxxvi. 1165).

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* The term aldol, although originally assigned by Wurtz to the compound under discussion, is most conveniently employed as a generic term to denote the hydroxyl derivatives of aldehydes, as these bodies exhibit properties which are in part characteristic of aldehydes, and in part of alcohols.

(1643) *Trichlorotetraldehyde* or *Trichlorobutyric Aldehyde:* $C_3H_4Cl_3.COH$.—The production of this compound from ethaldehyde by the action of chlorine has also already been alluded to, and the manner in which it is probably formed explained (p. 734). The aldehyde must be well cooled by a mixture of ice and salt, and the chlorine at first passed very slowly into it; when the gas ceases to be absorbed to any extent in the cold, the liquid is slowly heated on the water bath, but the action is almost complete in the cold. A small quantity of water is then added, and sufficient precipitated calcic carbonate nearly to neutralize the hydrochloric acid; a current of steam is subsequently passed through the liquid heated to about 110° (230° F.) in an oil bath. Crystalline *trichlorotetraldehydrol* or *trichlorobutaldehydrol* (p. 516), $C_3H_4Cl_3.CH(OH)_2$, then passes over, and may be purified by recrystallization from hot water; by distilling it in a current of hydrochloric acid gas, it is resolved into water and *trichlorotetraldehyde* or *trichlorobutyric aldehyde*,* $C_3H_4Cl_3.COH$.

Trichlorotetraldehyde is a colourless oil of peculiar odour, which boils at 164° (327°·2 F.). It combines more readily with alcohol to form the monethylin, $C_3H_4Cl_3.CH(OH).OC_2H_5$, than with water to form the aldehydrol, $C_3H_4Cl_3.CH(OH)_2$, alcohol decomposing the latter and converting it into the former. It also combines with other substances, entering into reaction with various bodies in the same way as trichlorethaldehyde, although less readily; moreover the resulting compounds do not crystallize with the same facility, and are less stable than those derived from trichlorethaldehyde. On oxidation with nitric acid, it yields trichlorobutyric acid, $C_3H_4Cl_3.COOH$, which is also obtained on passing chlorine into an aqueous solution of the aldehydrol; this acid is readily converted by the action of reducing agents into monochlorocrotonic acid, $C_3H_4Cl.COOH$, in which, however, the chlorine is only with difficulty displaced by hydrogen (Krämer and Pinner, *Ann. Chem. Pharm.*, clviii. 37; Pinner, *ibid.*, clxxix. 21; Sarnow, *ibid.*, clxiv. 93; Garzarolli-Thurnlak, *ibid.*, clxxxii. 81; Bischoff, *Deut. chem. Ges. Ber.*, vii. 632; Hepp, *ibid.*, vii. 1420).

The constitution of trichlorotetraldehyde has not yet been ascertained; from the manner in which it is formed, however, and the difficulty of displacing the third atom of chlorine, it may be inferred that the chlorine atoms are not all associated with the same carbon atom; the most probable formula being either $CH_3.CHCl.CCl_2.COH$ or $CH_3.CCl_2.CHCl.COH$.

(1644) *Isotetraldehyde; Isobutyric* or *Isobutylic Aldehyde:* $CH(CH_3)_2.COH$, may be obtained by distillation of a mixture of calcic isobutyrate and calcic formate, and by oxidation of isobutylic alcohol; in the latter case the product is contaminated with acetone as well as with isobutyric and acetic acids and isobutylic isobutyrate, and can only be separated from the acetone with difficulty (Krämer, *Deut. chem. Ges. Ber.*, vii. 252; Schmidt, *ibid.*, 1361). According to Linnemann and Zotta (*Ann. Chem. Pharm.*, clxii. 35), it is also formed on heating the dibromotetrane from isobutylene, $CBr(CH_3)_2.CH_2Br$, with water at 150°—160° (302°—320° F.). Isotetraldehyde is a colourless mobile liquid of pungent odour, soluble in 9 vols. of water at 20° (68° F.); it boils at 61° (141°·8 F.), and at 20° (68° F.) has the sp. gr. ·803. It readily forms a crystalline compound with hydric sodic sulphite; it is apparently much more stable in presence of potassic hydrate than the aldehydes previously described. Hydrochloric and sulphuric acids convert it into a crystalline polymeride, which melts at 60° (140° F.) and boils at 194° (381°·2 F.) (Barbaglia, *Deut. chem. Ges. Ber.*, v. 1052; Markownikoff, vi. 1176).

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* The compound thus obtained was long regarded as a chlorinated derivative of crotonic aldehyde, and termed croton chloral, but Pinner and Garzarolli-Thurnlak's recent experiments (*Deut. chem. Ges. Ber.*, viii. 1561; *Ann. Chem. Pharm.*, clxxxii. 181) have shown that this is not the case.

(1645) **Pentaldehydes**: $C_4H_7.COH$.—*Normal primary Pentaldehyde*: $CH_3.CH_2.CH_2.CH_2.COH$, obtained by distillation of a mixture of normal calcic pentylate (valerate) and calcic formate, boils at about 102° (215°·6 F.); it requires more than 30 times its volume of water to dissolve it, and readily furnishes a crystalline compound with hydric sodic sulphite (Lieben and Rossi, *Ann. Chem. Pharm.*, clix. 70).

Isopentaldehyde; Isovaleric or *Isoamylic Aldehyde; Valeral.*—None of the isopentaldehydes have been prepared in a pure state, but a mixture of *isopropacetaldehyde*, $CH(CH_3)_2.CH_2.COH$, and *methethacetaldehyde*, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}CH.COH$ —the so-called valeral—is formed on oxidizing the mixture of alcohols which constitute ordinary fermentation amylic alcohol, the alcohol being gradually added to a mixture of potassic dichromate, sulphuric acid and water, maintained at such a temperature that the products of oxidation at once distil over (comp. Krämer, *Deut. chem. Ges. Ber.*, vii. 254). To isolate the aldehydes, the product is neutralized with a solution of an alkali, and the remaining oil well shaken for some time with a concentrated solution of sodic hydric sulphite; the crystals which separate are then pressed between linen, washed with a little ether, dried, and then decomposed by distillation with a concentrated solution of sodic carbonate.

When purified by rectification, the mixture of aldehydes thus obtained boils at about 92° (197°·6 F.); it possesses a pungent odour, somewhat like that of apples, and excites coughing when inhaled. A number of derivatives have been prepared from this mixture of aldehydes. It is not acted upon by sulphuretted hydrogen alone, but when this gas is passed into its aqueous solution crystals of the corresponding thioaldehyde are obtained. This compound is insoluble in water, but dissolves in alcohol and ether, separating from the latter in white asbestos-like crystals, which melt at 69° (156°·2 F.); it may be volatilized unchanged in vacuo, its vapour density corresponding with the formula C_5H_8S. A corresponding selentetraldehyde may be obtained by the action of seleniuretted hydrogen (Schroeder, *Deut. chem. Ges. Ber.*, iv. 402).

When valeral is shaken with ammonia solution, the liquid soon solidifies to a mass of crystals of the composition $C_4H_7.CH(OH).NH_2 + 7OH_2$, insoluble in water, but soluble in alcohol and ether; when fused they decompose into water and the anhydrous compound $C_4H_7.CH(OH).NH_2$ (H. Strecker).

The anhydrous compound of valeral with ammonia, like that of ethaldehyde, may be volatilized unchanged in vacuo (Schroeder); it also resembles that of ethaldehyde in its behaviour with hydrocyanic acid, sulphuretted hydrogen and carbonic bisulphide, and when heated (comp. Hüfner, *Journ. pr. Chem.* [2], i. 6; Schroeder, *loc. cit.*; Lubavin, *ibid.*, v. 1101). Valeral also appears to enter into reaction with acid amides, to form compounds analogous to those derived from ethaldehyde; thus, on the addition of a minute quantity of hydrochloric acid to a solution of ethylic carbamate, $NH_2.COOC_2H_5$, in valeral, the liquid becomes warm, and soon solidifies to a mass of crystals of the compound $C_4H_9.CH(NH.COOC_2H_5)_2$ (Bischoff, *Deut. chem. Ges. Ber.*, vii. 633).

It is partially converted into a crystalline polymeride when allowed to remain for some time in contact with potassic carbonate (Bruylants, *ibid.*, viii. 414). Polymerides and condensation products, amongst others the aldehyde $C_{10}H_{18}O$, which bears to it the same relation that crotonic aldehyde bears to ethaldehyde, are also obtained on heating it alone or with sodium (Borodin), zinc (Riban), or lime (Fittig); and a hexchlorinated derivative of the aldehyde

$C_{10}H_{18}O$ is produced on saturating valeral with chlorine, a monochlorvaleral being formed when the action of chlorine is carried on for a short time only (Schroeder, *loc. cit.*). The aldehyde $C_{10}H_{18}O$ is also formed by the action of zincic ethide (Ricth and Beilstein), and of solid potassic hydrate at 0° (32° F.), on valeral (Borodin).

(1646) HEXALDEHYDES: $C_5H_{11}.COH$.—*Normal primary Hexaldehyde:* $CH_3.CH_2.CH_2.CH_2.CH_2.COH$, obtained by the distillation of a mixture of calcic normal hexylate (caproate) and calcic formate, is a colourless liquid, possessing the characteristic aldehyde odour, which boils at 127°·9 (262°·2 F.) under a pressure of 737·6 mm. of mercury, and at 0° (32° F.) has the sp. gr. ·8498. It oxidizes with remarkable facility on exposure to the air (Lieben and Janeck, *Ann. Chem. Pharm.*, clxxxvii. 130).

According to Pinner (*Deut. chem. Ges. Ber.*, x. 1052), a trichlorinated hexylic aldehyde is formed in small quantity in the preparation of trichlorobutyric aldehyde by the action of chlorine on ethaldehyde.

By distillation of the calcic salt of the caproic acid from optically inactive amylic alcohol with calcic formate, Rossi obtained an aldehyde boiling at 121° (249°·8 F.), which doubtless consisted chiefly, if not entirely, of the isoprimary hexaldehyde $(CH_3)_2CH.CH_2.CH_2.COH$.

(1647) NORMAL HEPTALDEHYDE; *Oenanthol:* $CH_3.(CH_2)_5.COH$.—This aldehyde is formed on oxidation of normal heptylic alcohol, and is the chief product of the dry distillation of castor oil: to prepare it, the oil is distilled as rapidly as possible, and the crude distillate is shaken with a concentrated solution of hydric sodic sulphite; the crystals which separate are purified by washing and pressing, and then decomposed by distillation with sodic carbonate solution, the distillation being best performed in a current of steam. It is a colourless oily liquid, of peculiar unpleasant smell, which boils at 154° (309°·2 F.). Heptaldehyde appears closely to resemble ethaldehyde in its behaviour with ammonia, and with amines and acid amides (comp. Schiff, *Ann. Chem. Pharm.*, *Sup.*, iii. 351; vi. 24; Medicus, *ibid.*, clvii. 44). By its action on urea under various conditions, Schiff (*ibid.*, cli. 186) has obtained a series of bodies formed by the separation of the oxygen of the aldehyde in combination with hydrogen from the urea: the diureide, $C_7H_{14}(NH.CO.NH_2)_2$, being produced on mixing alcoholic solutions of the two substances, and the triureide $CO\left\{\begin{array}{l}NH.C_7H_{14}(NH.CO.NH_2)\\NH.C_7H_{14}(NH.CO.NH_2)\end{array}\right.$ on triturating dry urea with heptaldehyde; still more complex bodies are readily formed on digesting these two compounds with the aldehyde. The di- and triureide are crystalline, but the more complex bodies are amorphous; they are destitute of basic properties, and also have lost the power possessed by urea of combining with metallic oxides; they are readily decomposed by dilute acids, the aldehyde and urea being regenerated.

(1648) HEXDECALDEHYDE; *Cetylic* or *Palmitic Aldehyde:* $C_{15}H_{31}.COH$.—According to Fridau and Dollfus (*Ann. Chem. Pharm.*, cxxxi. 287), this aldehyde is formed by oxidation of cetylic alcohol, and is a crystalline substance melting at about 50° (122° F.), almost insoluble in cold alcohol; it does not appear to combine with ammonia or acid sulphites, and has but very feeble reducing powers. If, however, the so-called cetylic alcohol is a mixture of homologous alcohols, as Heintz supposes, the aldehyde thus obtained is doubtless also a mixture.

§ II. ALDEHYDES OF THE $C_nH_{2n-1}.COH$ SERIES.

The only aldehydes of this series which have been investigated are acrylic aldehyde or acrolein, C_3H_4O, and crotonic aldehyde, C_4H_6O; it has been shown, however, that their homologues may be obtained from the aldehydes of the acetic series in the same manner that the latter is formed from ethaldehyde.

(1649) ACRALDEHYDE OR ACRYLIC ALDEHYDE; *Acrolein:* $C_2H_3.COH = CH_2 = CH.COH$.—This aldehyde appears to be the first product of the oxidation of the corresponding alcohol, allylic alcohol (comp. p. 466), but on account of the readiness with which it undergoes further oxidation, it cannot be prepared in this way. It is a constant product of the destructive distillation of all fats containing glyceric salts (glycerides), and is obtained in considerable quantity on distilling glycerol (glycerin) with bodies such as phosphoric anhydride or hydric potassic sulphate. The best method of preparing it is to distil a mixture of one part of dehydrated glycerol and two parts hydric potassic sulphate, collecting the distillate in a receiver containing a considerable quantity of calcic chloride and a little plumbic oxide, which is well cooled by a mixture of ice and salt; the distillate is then twice rectified from calcic chloride on the water bath (Hübner and Geuther, *Ann. Chem. Pharm.*, cxiv. 35; Aronstein, *ibid.*, *Sup.*, iii. 180). When the mixture is heated, the sulphate gradually dissolves, and chiefly water passes over; after a time the liquid froths considerably, but later on again boils tranquilly, and very little water is produced, the distillate consisting chiefly of acrolein. It would appear, therefore, that a glyceric potassic sulphate and water are first formed, and that the aldehyde is the product of the decomposition of the salt by heat. The calcic chloride and plumbic oxide are used with the object of at once removing the water and sulphurous acid from the distillate, in presence of which the acrolein rapidly undergoes change.

Acraldehyde is a mobile, colourless liquid, which exercises an intensely irritating action on the eyes and nose, a few drops diffused through a room rendering the atmosphere entirely insupportable; it boils at 52°·5 (126°·5 F.). It is lighter than water, of which about 40 parts are required to dissolve it; alcohol and ether dissolve it in all proportions. Pure acraldehyde may apparently be preserved unchanged, at least for a considerable period; but as ordinarily prepared it soon changes spontaneously into a white amorphous solid substance, called by Redtenbacher *disacryl*, which is probably a polymeride, and more rarely into a resinous body, the so-called *disacryl resin*. It is also very readily resinized by caustic alkalies (comp. Claus, *ibid.*, *Sup.*, ii. 120). Most oxidizing agents decompose it completely, but when it is carefully acted upon by argentic oxide, the silver salt of the corresponding acid, *acrylic acid*, $C_2H_3.COOH$, is produced. Nascent hydrogen converts it into allylic alcohol (Claus, *Deut. chem. Ges. Ber.*, iii. 404); at the same time a body of the composition $C_6H_{10}O_2 = 2C_3H_4O + H_2$ is produced (Linnemann, *Ann. Chem. Pharm., Sup.*, iii. 268), which is probably a dihydric alcohol bearing the same relation to the parent aldehyde that the butylenic glycol $CH_3.CH(OH).CH_2.CH_2(OH)$ bears to ethaldehyde.

If hydrochloric acid gas be passed into well-cooled acraldehyde, it is rapidly absorbed, the liquid becoming viscid; if the product be freed from the excess of acid by washing with cold water, and then exposed over sulphuric acid, it solidifies to a white crystalline mass of the composition $C_3H_5ClO = C_3H_4O + HCl$. This body melts at 32° (89°·6 F.); it is insoluble in water, but readily soluble in alcohol and ether, and if pure may be heated with these liquids, and even with dilute alkalies, without undergoing appreciable alteration. It reduces an ammoniacal silver solution also only very slowly. When distilled alone, it is resolved into acraldehyde and hydrochloric acid; concentrated hydrocloric acid, and dilute sulphuric and nitric acids also decompose it with formation of acraldehyde. When it is gently heated with about an equal weight of potassic hydrate, an oil passes over which soon solidifies to a mass of crystals of a polymeride of acraldehyde, the so-called *metacrolein.* This forms long needles of peculiar aromatic odour, which melt at 50° (122° F.); it is only very slightly soluble in hot water, but easily soluble in alcohol. When distilled alone, it is in great part reconverted into acraldehyde, which is also formed from it by the action of acids; it combines with hydrochloric acid, forming the compound above described (Geuther and Cartmell, *ibid.*, cxii. 3). From the reactions of the compound formed by the action of hydrochloric acid gas on acraldehyde, it appears probable that it is in reality a compound of metacrolein with hydrochloric acid, and that the first action of the latter is to polymerize the aldehyde—that is to say, that it is a polymeride of a chloropropaldehyde—probably of that having the formula $CH_3.CHCl.COH$.

Chlorine and bromine readily combine directly with acraldehyde, forming dichloro- and dibromo-derivatives of propaldehyde; the dibromide is converted into a dibromopropionic acid on oxidation with nitric acid, identical with that formed on oxidizing the dibromopropylic alcohol obtained by combining allylic alcohol with bromine (Linnemann and Penl, *Deut. chem. Ges. Ber.*, viii. 1097; Tollens, *ibid.*, 1448).

Acraldehyde is violently acted upon by phosphoric pentachloride; according to Geuther (*Jahresb.*, 1864, 333), the product is a mixture of the two dichloropropylenes $CH_2{=}CH.CHCl_2$ and $CH_2{=}CCl.CH_2Cl$.

It unites with a single molecule of acetic anhydride, but with two molecules of acetic chloride (Aronstein, *Ann. Chem. Pharm., Sup.*, iii. 193).

Acraldehyde combines readily with sodic hydric sulphite, forming the sodic salt of the oxypropanedisulphonic acid, $CH_3.CH(SO_3H).CH(OH).SO_3H$; this latter is decomposed by alkalies, and converted into propaldehydosulphonic acid, $CH_3.CH(SO_3H).COH$, which, on oxidation with argentic oxide, yields sulphopropionic acid, $CH_3.CH(SO_3H).COOH$, and when submitted to the action of nascent hydrogen is converted into oxypropanesulphonic acid, $CH_3.CH(SO_3H).CH_2(OH)$, identical with that formed by combining allylic alcohol with acid sulphites, and by the action of sulphuric anhydride on propylic alcohol (Müller, *Deut. chem. Ges. Ber.*, vi. 1441).

When a well-cooled solution of acraldehyde in at most an equal volume of absolute alcohol or ether is saturated with ammonia, and then mixed with ether, a white or yellowish amorphous precipitate of the composition $C_6H_9NO = 2C_3H_4O + NH_3 - OH_2$ is obtained, the compound corresponding to that formed by the direct union of ethaldehyde and ammonia being unknown. When this so-called acrolein-ammonia is submitted to dry distillation, it yields *picoline*, C_6H_7N, and other basic substances of unknown composition (Baeyer, *Ann. Chem. Pharm.*, clv. 283).

Aniline acts violently on acraldehyde, forming with it the compound $C_{18}H_{18}N_2 = 2C_3H_4O + 2NH_2.C_6H_5 - 2OH_2$ (Schiff). It is also readily acted upon by ammonic thiohydrate, and converted into *acrothialdin*, which, however, does not precisely correspond in composition to thialdin (p. 739), as it contains the elements of 3 mols. acraldehyde, 1 mol. ammonia, and 1 mol. sulphuretted hydrogen (Schiff). Cyanic acid converts acraldehyde into the compound $C_4H_7N_3O_2$, isologous with trigenic acid (Melms, *Deut. chem. Ges. Ber.*, iii. 759).

(1650) CROTONALDEHYDE or *crotonic aldehyde*: $CH_3.CH{=}CH.COH = C_4H_6O$—This aldehyde is best prepared by heating ethaldehyde mixed with a very small quantity of zincic chloride and a few drops of water in closed vessels such as soda-water bottles for one or two days at 100° (212° F.). The unchanged ethaldehyde is distilled off on the water bath, and a current of steam then passed through the residue, which carries over the crotonaldehyde; the latter partly swims as an oily layer on the surface of the water and partly dissolves in the water, from which it is separated by distillation, dried over calcic chloride and rectified.

Crotonaldehyde is a colourless liquid, moderately soluble in water, boiling at 104°—105° (219°·2—221° F.); at first it appears to have a pleasant fruity odour, which, however, afterwards becomes very pungent and similar to that of acraldehyde. It absorbs oxygen on exposure to the air, being converted into crotonic acid, $CH_3.CH{=}CH.COOH$, the silver salt of which is formed on warming its aqueous solution with argentic oxide; when oxidized by chromic or nitric acid, it yields chiefly acetic acid. Phosphoric pentachloride converts it into dichlorobutylene, $CH_3.CH{=}CH.CHCl_2$. Crotonaldehyde combines readily with hydrochloric acid gas, forming *chlorobutyric aldehyde*, C_4H_7ClO, which crystallizes in thick white needles, insoluble in water, melting at 96° (204°·8 F.); on boiling it with sulphuric acid, crotonaldehyde is re-formed; on oxidation with chromic acid it yields a considerable quantity of acetic acid, but no chlorobutyric acid is produced: hence it appears probable that, like the corresponding acraldehyde derivative, it may be formed from a polymeride of the parent aldehyde (Kekulé, *Ann. Chem. Pharm*, clxii. 96).

§ III. ALDEHYDES OF THE $C_nH_{2n-7}.COH$ SERIES.

The only aldehydes of this series at present known are the following:

Benzoic aldehyde	$C_6H_5.COH$.
Paratoluic or paramethylbenzoic aldehyde	$CH_3.C_6H_4.COH$.
α-Toluic or phenylacetic aldehyde	$C_6H_5.CH_2.COH$.
Cumic aldehyde	$C_3H_7.CH_4.COH$.
Sycocerylic aldehyde	

(1651) BENZOIC ALDEHYDE or BENZALDEHYDE; *Benzoyl hydride; Bitter almond oil*: $C_7H_6O=C_6H_5.COH$.—This aldehyde, which forms the principal constituent of the volatile oil of bitter almonds, obtained by distilling bitter almonds, the leaves of the cherry-laurel, peach and cherry kernels, &c., with water, may be obtained by various reactions.—(1) By the general method of distilling a mixture of calcic benzoate and formate. (2) By the action of oxidizing agents, not only on benzylic alcohol, $C_6H_5.CH_2(OH)$, but also on numerous other compounds, as stilbene, hydrobenzoin, mandelic acid, albumin, gelatin, &c. (3) By passing the vapour of benzoic chloride, $C_6H_5.COCl$, mixed with hydrogen over heated, finely divided palladium. (4) By the action of zinc and hydrochloric acid on benzoic cyanide, $C_6H_5.CO.CN$. (5) By the action of an alcoholic solution of potassic hydrate on (o–2) dichlorotoluene: $C_6H_5.CHCl_2+2KHO=C_6H_5.COH+2KCl+OH_2$; and also by heating this compound with water or metallic oxides; or by treating it with concentrated sulphuric acid, $C_6H_5.CHCl_2+2H_2SO_4=2HCl+C_6H_5.CH(SO_4H)_2$, and distilling the product with water. (6) By heating (o–1) monochlorotoluene or benzylic chloride with dilute nitric acid, or better with plumbic nitrate and water; much benzoic acid is formed at the same time, however.

Benzoic aldehyde is usually prepared from bitter almond oil, which besides the aldehyde contains hydrocyanic acid, &c., from which it may be purified by agitating the crude oil either with calcic hydrate, water, and ferrous chloride, and then rectifying; or with a concentrated solution of hydric sodic sulphite, after removal of the mother liquors, and purifying the crystals of the compound of the aldehyde with the sulphite which separate, by washing them with cold alcohol and recrystallising them from water; finally decomposing them by distillation with sodic carbonate and water. It has also been prepared on a commercial scale by the action of sulphuric acid on o–2 dichlorotoluene.

Pure benzoic aldehyde is a colourless liquid of high refractive power, having a pleasant aromatic odour, and burning taste, of the specific gravity 1·063 at 0° (32° F.). It boils at 180° (356°·7 F.). It requires 30 parts of water for solution, but is miscible in all proportions with alcohol or ether.

Benzoic aldehyde is a much more stable compound than the aldehydes of the series previously considered. It does not exhibit the least tendency to polymerize, nor does it undergo condensation in presence of minute quantities of foreign bodies; it also readily furnishes a number of well-characterized substitution derivatives. It gradually oxidizes on exposure to moist air, but does not reduce silver solutions; ordinary oxidizing agents converting it into benzoic acid, $C_6H_5.COOH$. The potassic salt of this acid is formed when it is heated with potassic hydrate, hydrogen being evolved; but if an alcoholic solution of potassic hydrate be employed, benzylic alcohol is also produced, the hydrogen resulting from the conversion of a portion of the aldehyde into benzoate reducing another portion of the aldehyde. Benzylic alcohol is also produced together with hydrobenzoin and isohydrobenzoin (1525) by the action of sodium amalgam, zinc and hydrochloric acid, &c., on benzaldehyde.

Chlorine and bromine readily act on benzaldehyde, displacing the hydrogen of the COH group; when chlorine is employed, together with benzoic or benzoyl chloride, $C_6H_5.COCl$, a compound formed by the union of benzoic chloride with benzaldehyde, $C_6H_5.CHCl(C_6H_5.COO)$, is also produced. It crystallizes in shining laminæ, and is decomposed by water into benzaldehyde, benzoic acid, and hydrochloric acid. Phosphoric pentachloride converts benzaldehyde into (0–2) dichlorotoluene, $C_6H_5.CHCl_2$.

By heating benzaldehyde with acetic anhydride at 150° (302° F.), it is converted into the diacetin, $C_6H_5.CH(C_2H_3O_2)_2$, which may also be obtained by heating (0–2) dichlorotoluene with argentic acetate: this compound crystallizes very readily, and melts at 45° (113° F.).

Benzaldehyde forms crystalline compounds with the acid sulphites of potassium and sodium, which are readily decomposed by acids and alkalies.

According to Herzfeld (*Deut. chem. Ges. Ber.*, x. 1271), benzaldehyde absorbs only about 11 per cent. of its weight of ammonia when submitted to the action of this gas; on exposing the product in vacuo over sulphuric acid it is gradually converted into hydrobenzamide: $C_{21}H_{18}N_2 = 3C_6H_5.COH + 2NH_3 - 3OH_2$. The latter compound is also slowly produced on digesting benzaldehyde with aqueous ammonia. It forms colourless crystals, insoluble in water, by heating with which it is gradually reconverted into its generators; hydrobenzamide is a perfectly neutral substance, but when heated alone for some time at about 130° (266° F.), or boiled with potassic hydrate solution, it is converted into an isomeric, powerfully basic substance, *amarine*, which is also formed on digesting benzaldehyde with an alcoholic solution of ammonia.

On digesting benzaldehyde with ammonic sulphide solution, a crystalline compound is obtained which apparently consists of thiobenzaldine, (?) $C_{21}H_{19}NS_2$.

Benzaldehyde resembles ethaldehyde in its behaviour with aniline; the two bodies at once enter into reaction with separation of water, forming a crystalline compound of the formula $C_{26}H_{22}N_2 = 2C_6H_5.COH + 2C_6H_5.NH_2 - 2OH_2$, which is entirely destitute of basic properties, however. It also acts in a similar manner on acid amides; thus a mixture of benzaldehyde and acetamide, heated to boiling for some time, yields the compound $C_6H_5.CH(NH.CO.CH_3)_2$; and analogous bodies may be prepared in a similar manner from the homologues of acetamide and from benzamide (Roth, *Ann. Chem. Pharm.*, cliv. 72). On adding a small quantity of hydrochloric acid to a solution of ethylic carbonate in benzaldehyde, the liquid at once solidifies to a mass of crystals of the compound $C_6H_5.CH(NH.COOC_2H_5)_2$ (Bischoff, *Deut. chem. Ges. Ber.*, vii. 634). On adding benzaldehyde to an alcoholic solution of urea, a mass of crystals of the diureide $C_6H_5.CH(NH.CO.NH_2)_2$ is soon formed; and by heating the dry substances together, the triureide and still more complex bodies are formed (Schiff).

Benzaldehyde unites with hydrocyanic acid to form the compound $C_6H_5.CH(OH).CN$, which is decomposed into its generators even by warm water; when digested with hydrochloric acid it is converted into mandelic acid, $C_6H_5.CH(OH).COOH$. This acid is most readily prepared by gently boiling a mixture of benzaldehyde, hydrocyanic acid, and dilute hydrochloric acid in a flask attached to a reversed condenser. If a mixture of benzaldehyde, hydrocyanic acid, and of a saturated solution of hydrochloric acid be allowed to stand for some time at the ordinary temperature, a crystalline substance of the formula $C_{15}H_{13}NO_3$ is obtained; it melts at 195° (385° F.); when heated with hydrochloric acid, it is decomposed with formation of benzaldehyde, mandelic acid, and ammonic chloride (Zinin, *Zeit. Chem.* [2], iv. 709), and probably therefore is a compound of the formula $C_6H_5.CH(OH).O.CH(CN).C_6H_5$. A still more complex compound, the so-called *benzimide* of Laurent, $C_{23}H_{18}N_2O_2$, is said to be formed when a mixture of benzaldehyde and hydrocyanic acid is heated with an alcoholic solution of potassic hydrate. In presence of a dilute alcoholic solution of potassic cyanide, benzaldehyde undergoes a most remarkable transformation, being converted into benzoin, $C_6H_5.CO.CH(OH).C_6H_5$, which it may be supposed is formed by condensation of 2 mols. of the compound $C_6H_5.CH(OH).CN$ (comp. Zincke, *Deut. chem. Ges. Ber.*, ix. 1772).

Benzaldehyde appears to enter into reaction with all the phenols in a similar manner, first forming a compound containing the elements of a molecule of aldehyde and of a molecule of the phenol, from which, in the second stage of the reaction, a more complex substance results by the union of two molecules with separation of the elements of a molecule of water. Thus by the action of phenol on benzaldehyde in presence of sulphuric acid, probably the compound $C_6H_5.CH(OH).C_6H_4.OH$ is first produced, two molecules of which then unite with separation of the elements of a molecule of water. Similarly, when a mixture of benzaldehyde and pyrogallol is heated, a reddish-brown resinous mass is obtained, consisting chiefly of a difficultly-crystallizable resinous body of the composition $C_{26}H_{22}O_7$ and a red oxidation product; the former substance is at once obtained in a pure state on mixing a cold solution of pyrogallol in hydrochloric acid with a cold, well-incorporated mixture of benzaldehyde and a large quantity of hydrochloric acid: after a few seconds the solution becomes turbid, and deposits the perfectly colourless substance. On heating the product, a part becomes red, and a part is converted into a crystalline substance of the same composition: the latter is at once obtained when very concentrated solution of hydrochloric acid is added in small portions at a time to a boiling solution of pyrogallol and benzaldehyde in a large quantity of absolute alcohol until the precipitate no longer increases in amount (Baeyer, *Deut. chem. Ges. Ber.*, v. 280). Probably in this case the first action is between the pyrogallol and the compound of the aldehyde with hydrochloric acid; thus:

$$C_6H_5.CHCl(OH) + C_6H_3(OH)_3 = C_6H_5.CH(OH).C_6H_2(OH)_3 + HCl.$$

It was first shown by Bertagnini (*Ann. Chem. Pharm.*, c. 125), and afterwards confirmed by Kraut (*ibid.*, cxlvii. 110), that when benzaldehyde is heated for some hours with acetic chloride at 120°—130° (248°—266° F.), a viscid mass is obtained, from which water extracts a small quantity of cinnamic or phenacrylic acid, $C_6H_5.CH{=}CH.COOH$. The formation of this acid is perhaps brought about in consequence of the hydrochloric acid contained in the acetic chloride combining with the aldehyde, thus producing the compound $C_6H_5.CHCl(OH)$, which then enters into reaction with the acetic chloride to form cinnamic chloride, water, and hydrochloric acid: $C_6H_5.CHCl(OH) + CH_3.COCl = C_6H_5.CH{=}CH.COCl + HCl + OH_2$; or it may be supposed that a compound of the aldehyde and acetic chloride is first formed, which then enters into reaction with acetic chloride, thus: $C_6H_5.CHCl(C_2H_3O_2) + CH_3.COCl = C_6H_5.CH{=}CH.COCl + HCl + C_2H_4O_2$. Fittig and Bieber subsequently obtained the homologous acid, phenangelic acid, $C_{11}H_{12}O_2$, by heating a mixture of benzaldehyde and butyric chloride. Perkin, however, has recently shown (*Journ. Chem. Soc.*, 1877, i. 389) that cinnamic acid and its homologues may be far more readily obtained by heating a mixture of benzaldehyde and acetic anhydride or the homologous anhydrides, with the sodic salt of the acid of the acetic series corresponding to the anhydride employed, benzaldehyde yielding as much as 84 per cent. of its weight of cinnamic acid; the formation of cinnamic acid from benzaldehyde in this manner has already been discussed (p. 722).

(1652) *Thiobenzaldehydes.*—When heated with an alcoholic solution of potassic thiohydrate, (0–2) dichlorotoluene, $C_6H_5.CHCl_2$, is converted into a body of the composition C_7H_6S, soluble in alcohol and ether, and which crystallizes from the latter in four-sided prisms melting at about 69° (156°·2 F.); it decomposes when distilled, and on oxidation with dilute nitric acid apparently yields a thiobenzoic acid, (?) $C_6H_5.CSOH$ (Fleischer, *Ann. Chem. Pharm.*, cxl. 234).

According to Laurent (*Ann. Ch. Phys.* [3], i. 291), a body which also has the composition of thiobenzaldehyde is obtained on mixing alcoholic solutions of benzaldehyde and ammonic thiohydrate, but this is amorphous and insoluble in alcohol, and only softens when heated at 90°—95° (194°—203° F.).

Klinger has recently found (*Deut. chem. Ges. Ber.*, ix. 1895), that when sulphuretted hydrogen is passed into an alcoholic solution of benzaldehyde, according to the concentration, either an amorphous reddish flocculent substance, or an oil which soon solidifies and consists of essentially the same substance, is obtained. When purified by washing with alcohol and sodic carbonate solution, solution in benzene or chloroform, and precipitation by alcohol, it forms an amorphous mass of the composition C_7H_6S, easily soluble in benzene and chloroform, and somewhat difficultly soluble in hot alcohol, which softens at about 84° (183°·2 F.), and decomposes when heated to a higher temperature. Acetic chloride converts this substance into a crystalline polymeride, easily soluble in hot acetic acid, from which it separates on cooling in glistening white needles melting at 225° (437° F.); when heated with metallic copper it is almost entirely converted into stilbene, $C_6H_5.CH{=}CH.C_6H_5$.

(1653) HALOID AND NITRO-DERIVATIVES OF BENZALDEHYDE.—Haloid derivatives have not yet been directly prepared in a pure state from benzaldehyde, but several have been obtained from chlorinated derivatives of (0–1) chlorotoluene or benzylic chloride by boiling them with plumbic nitrate and water, and from chlorinated derivatives of (0–2) dichlorotoluene by heating them with water alone at high temperatures. *Parachlorobenzaldehyde*, $C_6H_4Cl.COH$, prepared from parachlorobenzylic chloride, is liquid, and very readily oxidizes to parachlorobenzoic acid on exposure to the air (Beilstein and Kuhlberg, *Ann. Chem. Pharm.*, cxlvii. 352). An isomeric orthochlorobenzaldehyde is formed by distilling salicylic aldehyde, $C_6H_4(OH).COH$, with phosphoric pentachloride, and heating the resulting (1–2) trichlorotoluene with water; it boils at 210° (410° F.). Di- and trichlorobenzaldehyde are crystalline.

Nitric acid alone appears always to oxidize benzaldehyde to benzoic acid, but unless the very strongest acid be used, the action takes place but slowly in the cold; if, however, benzaldehyde be mixed with 20 times its volume of a mixture of 1 vol. ordinary concentrated nitric acid and 2 vols. concentrated sulphuric acid which is kept cold, the product is a mass of crystals saturated with an oil. The former consists of metanitrobenzoic aldehyde, $C_6H_4(NO_2).COH$, which crystallizes from alcohol in small white needles, melting at 58° (136°·4 F.); this compound appears closely to resemble benzaldehyde in its reactions (Bertagnini, *Ann. Chem. Pharm.*, lxxix. 259; Lippmann and Hawliczek, *Deut. chem. Ges. Ber.*, ix. 1463). The oil which accompanies the crystals may be purified by shaking with a solution of hydric sodic sulphite, which combines with the aldehyde, and extracting the liquid with ether; on distilling off the ether an oil remains, which may be freed from water by heating in vacuo at 105°—110° (221°—230° F.); if heated higher it decomposes. This product has the same empirical composition as nitrobenzaldehyde, but on oxidation it yields benzoic acid without evolution of carbonic anhydride, and therefore is probably formed from benzaldehyde by the displacement of hydrogen in the COH group by NO_2 (Lippmann and Hawliczek).

(1654) HYDROXYL DERIVATIVES OF BENZALDEHYDE; *Phenaldols.*—Several aldehydes are known, formed from benzaldehyde by the displacement of hydrogen atoms in the C_6 group by the group OH, which exhibit certain of the properties characteristic of the phenols as well as the properties of aldehydes. Two of these compounds are of especial interest, as they are closely related to a number of substances which occur naturally in plants. We are acquainted with the following "phenaldols":

Orthoxybenzaldehyde or salicylic aldehyde . . . Paroxybenzaldehyde	$C_6H_4(OH).COH$
Metoxyparoxybenzaldehyde or protocatechuic aldehyde	$C_6H_3(OH)_2.COH$

(1655) ORTHOXYBENZALDEHYDE; *Salicylic aldehyde, salicylol*, or *salicylous acid:* $C_7H_6O_2 = C_6H_4(OH).COH$ (OH : COH = 1 : 2).—This aldehyde was discovered by Pagenstecher in 1835, who obtained it by distilling the flowers of meadow sweet, *Spiræa ulmaria*, with water; it may be procured from other species of spiræa, and also from the larvæ of *Chrysomela populi*, and from the beetles themselves by distillation with water. It is formed on oxidation of the corresponding alcohol, saligenol (saligenin), $C_6H_4(OH).CH_2(OH)$, and also by the action of oxidizing agents on the glucosides which yield this alcohol—viz., populin and salicin, and, in fact, is usually prepared from the latter: 2 parts of salicin, 2 of potassic dichromate and 16 of water are placed in a retort, and a mixture of 3 parts of sulphuric acid and eight of water added; a slight evolution of gas takes place during 30 to 45 minutes, and the liquid becomes green. When the evolution of gas ceases, heat is applied and the aldehyde distilled over; the oil is then separated from the water, and the portion which remains dissolved extracted with ether. By this process salicin yields about 24 per cent. of its weight of the aldehyde.

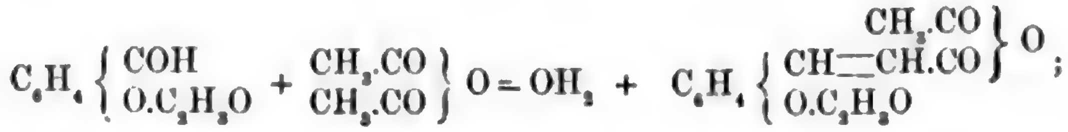
The most interesting method of preparing salicylic aldehyde, however, is by the action of trichloromethane (chloroform) on sodium phenol (comp. p. 716): 20 parts of phenol are dissolved in a solution of 60 parts of sodic hydrate in at least twice the weight of water heated to 56°—60° (122°—140° F.), and slightly more than the equivalent amount of trichloromethane is gradually added, the mixture being constantly agitated; the reaction is completed by boiling the mixture for half an hour, the excess of chloroform is then distilled off, a slight excess of sulphuric or hydrochloric acid added, and the salicylic aldehyde together with the unattacked phenol distilled off by passing a current of steam through the liquid. To separate the aldehyde from the phenol, the mixture is dissolved in ether, and the former extracted with a solution of hydric sodic sulphite, &c.

Salicylic aldehyde is a colourless oily liquid, of pleasant aromatic odour, boiling at about 196° (384°·8 F.), of the sp. gr. 1·173 at 15° (59° F.). It is moderately soluble in water, and miscible with alcohol and ether in all proportions; its solutions are coloured deep violet by ferric chloride. On oxidation it is converted into salicylic acid. It combines with the acid sulphites, forming crystalline compounds which are readily decomposed by acids with separation of the unaltered aldehyde. It is acted upon by aniline and by urea in the same manner as benzaldehyde. With potassic chlorate and hydrochloric acid, it yields tetrachloroquinone, $C_6Cl_4O_2$. Salicylic aldehyde readily dissolves in solutions of the alkalies, and even decomposes carbonates, forming crystalline metallic derivatives, such as $C_6H_4(OK).COH$ and $C_6H_4(ONa).COH$, from which other metallic derivatives may be obtained by double decomposition; crystalline metallic derivatives consisting of a molecule of the potassium or sodium derivative united with a molecule of the aldehyde are also known. Ammonia combines with salicylic aldehyde, probably forming the ammonium derivative, $C_6H_4(ONH_4).COH$; on heating this compound, water and hydrosalicylamide, $C_{21}H_{18}N_2O_3 = 3C_7H_6O_2 + 2NH_3 - 3OH_2$, are formed. The hydrogen of the OH group may also be displaced by both positive and negative organic radicles. By heating the sodium derivative $C_6H_4(ONa).COH$ with methylic iodide, *methylsalicylol* or *orthomethoxybenzaldehyde*, $C_6H_4(OCH_3).COH$, is produced, and the corresponding ethyl derivative may be formed by the action of ethylic iodide; both are colourless oils, which boil, the former at about 238° (460°·4 F.), the latter at about 248° (478°·4 F.); they form crystalline compounds with the acid sulphites, and enter into reaction with ammonia, the hydramide, $C_{27}H_{30}N_2O_3$, derived from the latter as well as that derived from the former, undergoing conversion into an isomeric basic substance when heated (Perkin, *Journ. Chem. Soc.*, xx. 418). By the action of benzylic chloride on the sodium derivative of salicylic aldehyde, a benzyl derivative is obtained corresponding in its properties to the methyl and ethyl derivatives (Perkin, *ibid.*, xxi. 122).

Mono- and di-chlorinated and brominated derivatives of salicylic aldehyde have been prepared by the action of chlorine and bromine, and a mononitro-derivative by the action of nitric acid; by the action of pentachloride of phosphorus, the dichlororthocresol, $C_6H_4(OH).CHCl_2$, and 1–2 trichlorotoluene are formed.

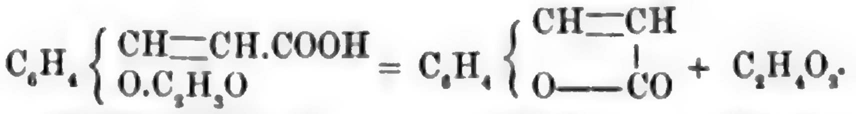
When salicylic aldehyde is mixed with acetic chloride, hydrochloric acid is evolved, and the liquid on cooling deposits crystals of a body of the composition $C_{14}H_{10}O_3$, which Perkin represents by the formula $O\left\{\begin{matrix}C_6H_4.COH\\C_6H_4.COH\end{matrix}\right.$:—Considering the difficulty with which the phenols form ethers, however, this formula appears scarcely probable. The product in question is, perhaps, a condensation product of the formula $C_6H_4(OH).CH{=}C_6H_3(OH).COH$. It is also obtained by the action of benzoic and succinic chlorides. It does not combine with acid sulphites, and when heated with acetic chloride is converted into a non-distillable oil (Perkin).

If, however, acetic anhydride be added to the sodium derivative of salicylic aldehyde suspended in pure dry ether, action gradually takes place, and acetosalicylic aldehyde, $C_6H_4(C_2H_3O_2).COH$, is produced, together with sodic acetate; it is a crystalline substance which melts at 37° (98°·6 F.), and boils at about 253° (487°·4 F.) with but very little decomposition. It combines with the acid sulphites; when heated with acetic anhydride at 150° (302° F.), it combines with it, forming the compound $C_6H_4(C_2H_3O_2).CH(C_2H_3O_2)_2$, which decomposes into its generators on distillation (Perkin, *ibid.*, xxi. 182). The corresponding compound of salicylic aldehyde, $C_6H_4(OH)\ CH(C_2H_3O_2)_2$, is obtained by heating a mixture of the latter with acetic anhydride at 150° (302° F.); when distilled it partially decomposes, and on heating with water, it yields acetic acid and salicylic aldehyde. The methyl and ethyl derivatives of salicylic aldehyde also combine with acetic anhydride in a precisely similar manner (Perkin, *ibid.*, xx. 586). If instead of acting upon the sodium derivative of salicylic anhydride with acetic anhydride in presence of ether the two substances be simply mixed together, the sodium derivative soon dissolves, much heat being developed; and if the mixture be boiled for a few minutes, then poured into water, and the oil which separates be distilled, at first small quantities of acetic acid and of unaltered aldehyde pass off, after which nearly pure *coumarin*, $C_9H_6O_2$, distils over at about 290° (554° F.) (Perkin, *ibid.*, xxi 53). Coumarin is contained in the tonka bean, which derives its sweet odour from it, and is also present in woodruff, *Asperula odorata*, in the flowers of sweet vernal grass, *Anthoxanthum odoratum*, and in other plants. Tiemann and Herzfeld have recently shown (*Deut. chem. Ges. Ber.*, x. 283) that its formation in the above manner is preceded by that of acetorthocoumaric acid. Doubtless the salicylic aldehyde is, in the first place, converted into the acetyl derivative $C_6H_4(O.C_2H_3O).COH$; this product then either enters into reaction with a molecule of acetic anhydride to form the mixed anhydride of acetic and orthocoumaric acids:



$$C_6H_4\left\{\begin{matrix}COH\\O.C_2H_3O\end{matrix}\right. + \left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O = OH_2 + C_6H_4\left\{\begin{matrix}\left.\begin{matrix}CH_3.CO\\CH{=\!=}CH.CO\end{matrix}\right\}O\\O.C_2H_3O\end{matrix}\right.;$$

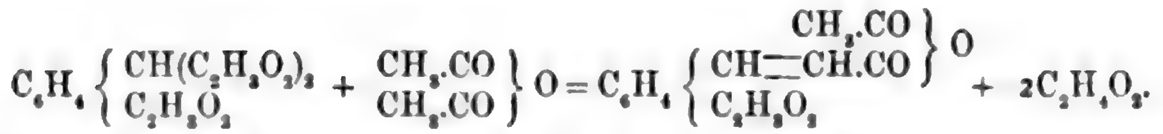
or it combines with the anhydride, forming $C_6H_4(O.C_2H_3O).CH(O.C_2H_3O)_2$, and the mixed anhydride is produced by the action of this acetodiacetin on a molecule of acetic anhydride. On pouring into water, the anhydride is decomposed into acetic and acetorthocoumaric acids; on distilling the latter, it breaks up into coumarin and acetic acid:



$$C_6H_4\left\{\begin{matrix}CH{=\!=}CH.COOH\\O.C_2H_3O\end{matrix}\right. = C_6H_4\left\{\begin{matrix}CH{=\!=}CH\\ \quad\ \ |\\O{-\!-}CO\end{matrix}\right. + C_2H_4O_2.$$

Acetorthocoumaric acid. Coumarin. Acetic acid.

The presence of sodic acetate is necessary to the formation of coumarin, which is not produced by merely heating together salicylic aldehyde and acetic anhydride; it apparently plays the part of a dehydrating agent, but it is difficult to explain the precise manner in which it acts: if, however, it be supposed that the mixed anhydride of acetic and orthocoumaric acid which is produced results from the action of the acetic anhydride on the acetodiacetin, $C_6H_4(C_2H_3O_2).CH(C_2H_3O_2)_2$, it is not improbable that the function of the sodic acetate in inducing the formation of this anhydride is the consequence of the tendency which this salt possesses to combine with acetic acid:



$$C_6H_4\left\{\begin{matrix}CH(C_2H_3O_2)_2\\ C_2H_3O_2\end{matrix}\right. + \left.\begin{matrix}CH_3.CO\\ CH_3.CO\end{matrix}\right\}O = C_6H_4\left\{\begin{matrix}\left.\begin{matrix}CH_3.CO\\ CH{=}CH.CO\end{matrix}\right\}O\\ C_2H_3O_2\end{matrix}\right. + 2C_2H_4O_2.$$

Perkin has shown that by employing the homologues of acetic anhydride, a series of bodies homologous with coumarin may be obtained, and also that orthomethoxybenzoic aldehyde and the lower haloid derivatives of salicylic aldehyde enter into reaction with the anhydrides of the acetic series in the same manner as salicylic aldehyde.

From Baeyer's experiments it appears that salicylic aldehyde resembles benzaldehyde in its action on phenols in presence of hydrochloric and sulphuric acids. According to Liebermann and Schwarzer (*Deut. chem. Ges. Ber.*, ix. 800), salicylic aldehyde is rapidly converted into a red solid substance, closely resembling the so-called rosolic acid in its properties, when warmed with concentrated sulphuric acid; and by the action of the acid on a mixture of salicylic aldehyde and phenol, "rosolic acid": $C_{20}H_{14}O_3 = C_6H_6O + 2C_7H_6O_2 - 2OH_2$, identical with that produced on heating phenol with oxalic and sulphuric acids, is obtained. From this it appears probable that in the formation of "rosolic acid" from phenol and oxalic acid, salicylic aldehyde is first produced by the action on the phenol in presence of the sulphuric acid of the formic acid resulting from the decomposition of the oxalic acid: $C_6H_5.OH + H.COOH = C_6H_4(OH).COH + OH_2$.

(1656) **Paroxybenzoic aldehyde**: $C_6H_4(OH).COH$, the isomeride of salicylic aldehyde, is obtained on heating paramethoxybenzoic or anisic aldehyde, $C_6H_4(OCH_3).COH$, with hydrochloric acid at 200° (392° F.), for three or four hours (Bucking, *ibid.*, ix. 527), but is most readily prepared from phenol by the action of chloroform in presence of potassic or sodic hydrate, 100 grams of phenol yielding, according to Tiemann and Herzfeld (*ibid.*, x. 63), 10 grams of the pure aldehyde. It crystallizes in slender needles, which in the dry state melt at 112° (233°·6 F.), but under water at about 60° (140° F.). It has a pleasant aromatic odour, and dissolves readily in alcohol and ether, but not in cold water, although hot water dissolves it more readily; its aqueous solution is coloured a dirty violet by ferric chloride. It forms crystalline alkali-metal derivatives, and an oily ammonium derivative, which soon loses ammonia on exposure to the air; aniline enters into reaction with it to form a crystalline body of the composition $C_{13}H_{11}NO = C_7H_6O_2 + C_6H_7N - OH_2$ (Herzfeld, *ibid.*, x. 1267). It combines with the acid sulphites, and reduces an ammoniacal solution of a silver salt, but it is not easily oxidized by the ordinary oxidizing agents. Fused potassic hydrate, however, readily converts it into potassic paroxybenzoate. When submitted to the action of nascent hydrogen it furnishes a mixture of *paroxybenzylic alcohol*, $C_6H_4(OH).CH_2.OH$, and of *hydroparoxybenzoin*, $[C_6H_4(OH).CH.OH]_2$; apparently there is no isomeride of the latter formed. By the action of acetic anhydride on its potassium derivative, acetoparoxybenzoic aldehyde, $C_6H_4(C_2H_3O_2).COH$, is formed; and by boiling it with acetic anhydride the aceto-diacetin, $C_6H_4(C_2H_3O_2).CH(C_2H_3O_2)_2$, is produced. If the sodium derivative of paroxybenzoic aldehyde be boiled with acetic anhydride and sodic acetate, the acetyl derivative of paracoumaric acid, $C_6H_4(OH).CH{=}CH.COOH$, is formed.

(1657) **ParametHoxybenzoic or anisic aldehyde**; *hydride of anisyl*: $C_6H_4(OCH_3).COH$, may be obtained by digesting a mixture of paroxybenzoic aldehyde, potassic hydrate, methylic iodide, and methylic alcohol (Tiemann and Herzfeld), but is usually prepared by the oxidation of oil of anise (comp. Rossel, *Ann. Chem. Pharm.*, cli. 25). It is a colourless liquid of aromatic odour, boiling at about 250° (482° F.), which rapidly absorbs oxygen from the atmosphere, being converted into anisic or paramethoxybenzoic acid; when heated with an alcoholic solution of potassic hydrate, it yields a mixture of potassic anisate and of anisic alcohol. In other respects it most closely resembles benzoic aldehyde: forming a crystalline compound with hydric sodic sulphite; being converted into *hydranisoin* and *isohydranisoin*, the methoxy-derivatives of hydro- and isohydrobenzoin, by the action of nascent hydrogen; into anishydramid by the action of ammonia; and into anisoin, the analogue of benzoin, by treatment with potassic cyanide solution. When heated with acetic chloride, it is converted into a humus-like substance (Rossel). According to Perkin, it yields paramethoxyphenacrylic acid, $C_6H_4(OCH_3).CH{=}CH.COOH$, when heated with sodic acetate and acetic anhydride; and by employing propionic and butyric anhydrides the homologous paramethoxyphenylcrotonic and phenylangelic acids may be obtained. These acids, on distillation, are decomposed with evolution of carbonic anhydride, paramethoxyphenylcrotonic acid, $C_6H_4(OCH_3).C_3H_4.COOH$, yielding, moreover, a body which is apparently identical with anethol, $C_6H_4(OCH_3).C_3H_5$, the chief constituent of oil of anise.

(1658) PARAMETADIOXYBENZOIC or PROTOCATECHUIC ALDEHYDE: $C_7H_6O_3 = C_6H_3(OH)_2.COH$ (COH : OH : OH = 1 : 3 : 4).—Considerable interest attaches to this aldehyde on account of its relation to vanillin and piperonal. It is formed from the latter by heating it with dilute hydrochloric acid, carbon being separated; also on warming dichlorpiperonal with water, and on heating the former with hydrochloric acid. It crystallizes from water in flat crystals, which are usually arranged in concentric groups; it melts at 150° (302° F.), at which temperature, however, it begins to decompose. Its aqueous solution becomes of an intense pure green colour on the addition of ferric chloride; on the addition of a small quantity of sodic carbonate solution, the colour changes to violet, whilst a larger quantity renders it a magnificent red. If dissolved in an excess of sodic carbonate solution, it may be extracted by ether, but not if dissolved in a solution of hydric sodic sulphite. It exhibits powerful reducing properties, and when carefully fused with potassic hydrate, it is oxidized to protocatechuic acid, $C_6H_3(OH)_2.COOH$ (Fittig and Remsen, *Ann. Chem. Pharm.*, clix. 148; clxviii. 93).

(1659) PAROXYMETAMETHOXYBENZOIC ALDEHYDE; *methylprotocatechuic aldehyde;* or *vanillin:* $C_8H_8O_3 = C_6H_3(OH)(OCH_3).COH$ ($COH:OCH_3:OH$ = 1:3:4).—The formation of this compound from coniferin, a glucoside occurring in the cambium of coniferous trees, has already been described (p. 691); it is also obtained on carefully heating opianic acid, $C_6H_2(OCH_3)_2(COH).COOH$, with a concentrated solution of zincic chloride (Armstrong), and it is to this substance that vanilla, the fruit of a climbing orchidaceous plant, *Vanilla planifolia*, growing wild in Mexico, Brazil, and other tropical countries, owes its peculiar pleasant aromatic odour. It forms colourless needle-like crystals, soluble with difficulty in cold, but easily in hot water, and readily soluble in alcohol and ether; it melts at about 80° (176° F.), and if carefully heated may be sublimed unchanged. Its aqueous solution is strongly acid, and it furnishes a series of metallic derivatives of the general formula $C_6H_3(OR')(OCH_3).COH$, which mostly crystallize well. By digesting the potassic derivative with methylic alcohol and methylic iodide, parametadimethoxybenzoic aldehyde, $C_6H_3(OCH_3)_2.COH$, is produced; whilst, if ethylic alcohol and iodide be employed, the corresponding parethoxymetamethoxybenzoic aldehyde, $C_6H_3(OC_2H_5)(OCH_3).COH$, is obtained. The former crystallizes in colourless needles, melting between 15° and 20° (59° and 68° F.), and boils at 285° (545° F.) without decomposition; on oxidation it yields the corresponding dimethoxybenzoic acid. The latter crystallizes in large prismatic tables, melting at 65° (149° F.), and yields an ethmethoxybenzoic acid on oxidation, identical with that obtained on oxidation of ethyleugenol (1603). When vanillin is submitted to the action of bromine or of iodine, it is converted into bromo- and iodovanillin, $C_8H_7BrO_3$ and $C_8H_7IO_3$, both of which are crystalline. By digesting it for some time with dilute hydrochloric acid at 200° (392° F.), protocatechuic aldehyde and methylic chloride are produced; and when it is heated with potassic hydrate, the potassic salt of protocatechuic acid is obtained. It yields a mixture of *vanillylic alcohol*, $C_6H_3(OH)(OCH_3).CH_2.OH$, and of *hydrovanilloin*, $(C_7H_7O_2.CH.OH)_2$, when submitted to the action of nascent hydrogen; the former is easily soluble in ether, alcohol, and warm water, and like saligenol (saligenin) is converted into an insoluble resinous compound analogous to saliretin when treated with dilute acids; the latter is almost insoluble in cold water, very slightly soluble in boiling water or alcohol, and insoluble in ether. Vanillin is not extracted by ether when dissolved in a solution of hydric sodic sulphite (Tiemann and Haarmann, *Deut. chem. Ges. Ber.*, vii. 608; Tiemann, *ibid.*, viii. 1123; ix. 409.

(1660) PARAMETAMETHYLENOXYBENZOIC ALDEHYDE; *methyleneprotocatechuic* or *piperonylic aldehyde; piperonal:* $C_8H_6O_3 = C_6H_3(COH)\left\{\begin{matrix}O\\O\end{matrix}\right\}CH_2$. —This aldehyde is formed on oxidation of piperic acid (q. v.), $C_{12}H_{10}O_4$, with potassic permanganate. It is only sparingly soluble in cold, but more readily in hot water, from which it crystallizes on cooling in large, colourless, transparent, lustrous prisms, having an odour resembling that of coumarin; it melts at 37° (98°·6 F.), and boils at 263° (505°·4 F.). It forms a crystalline compound with hydric sodic sulphite, and on oxidation, it is converted into piperonylic acid, $C_8H_6O_4$. When submitted to the action of nascent hydrogen, it yields *piperonylic alcohol*, $C_8H_8O_3$, together with *hydropiperoin* and *isohydropiperoin*, $C_{16}H_{14}O_6$, two isomeric dihydric alcohols which manifest the closest resemblance in their properties to hydrobenzoin and isohydrobenzoin (1525); piperonylic alcohol melts at 51° (123°·8 F.), hydropiperoin at 202° (395°·6 F.), and isohydropiperoin at 135° (275° F.); of the last two compounds the latter is far more soluble in water and alcohol, and both are more soluble than the monohydric alcohol. When piperonal is acted upon by phosphoric pentachloride, it yields either piperonal chloride, $C_7H_5O_2.CHCl_2$, or dichloropiperonal chloride, $C_7H_3Cl_2O_2.CHCl_2$, according to the proportions employed; both these compounds are liquids, and boil respectively at 240°—250° (464°—482° F.) and 280° (536° F.); the former in contact with water is reconverted into the aldehyde, whilst the latter yields a dichlorinated derivative of the aldehyde, $C_7H_3Cl_2O_2.COH$, which doubtless has the formula $C_6H_3(COH)\left\{\begin{matrix}O\\O\end{matrix}\right\}CCl_2$, as on warming with water it completely decomposes into protocatechuic aldehyde, carbonic anhydride, and hydrochloric acid:

$$C_6H_3(COH)\left\{\begin{matrix}O\\O\end{matrix}\right\}CCl_2 + 2OH_2 = C_6H_3(OH)_2.COH + CO_2 + 2HCl.$$

The formula assigned by Fittig and Remsen to piperonal is placed beyond doubt by their discovery that piperonylic acid may be synthesized by heating protocatechuic acid with potassic hydrate and methylenic iodide, CH_2I_2 (*Ann. Chem. Pharm.*, clii. 25; clix. 129; clxviii. 93).

(1661) *Homologues of benzoic aldehyde.*—Two aldehydes derived from toluene or methylbenzene and one from (?) isopropylbenzene are known; by boiling sycocerylic alcohol (1482) with a dilute aqueous solution of chromic acid (De la Rue and Müller, *Journ. Chem. Soc.*, v. 62) obtained, on one occasion, a crystalline neutral substance, which probably was the corresponding aldehyde. *Paratoluic* or *paramethylbenzoic aldehyde*, $CH_3.C_6H_4.COH$, and *α toluic, phenylacetic* or *phenethaldehyde*, $C_6H_5.CH_2.COH$, are respectively obtained by distilling the calcic salts of paratoluic and phenylacetic acids with calcic formate. The former is an oily liquid, boiling at 204° (399°·2 F.); the latter is solid, but has not been obtained in a crystalline state, separating from its ethereal solution as a gelatinous mass (Radziszweski).

Cumic or *cuminic aldehyde*, or *cuminol*, $C_3H_7.C_6H_4.COH$, is contained together with cymene in the essential oil of cumin (*Cuminum cyminum*), and also in that of the water hemlock (*Cicuta virosa*). It may be separated by shaking the oil with a concentrated solution of hydric sodic sulphite, and then decomposing the crystalline compound which separates by sodic carbonate, after purification in the usual way by pressure and washing with alcohol. Cumic aldehyde is a colourless oil, having a powerful odour of cumin, boiling at about 237° (458°·6 F.). In all respects it exhibits the closest resemblance to benzoic aldehyde, absorbing oxygen on exposure to moist air, and being converted into cumic acid, which is also formed from it by the action of the weaker oxidizing agents; when boiled with chromic acid, however, it yields terephthalic acid, which is a proof that the groups C_3H_7 and COH are relatively in the positions 1–4. It is generally supposed that the group C_3H_7 has the constitution of isopropyl, $CH(CH_3)_2$, as according to the investigation of Fittig, Ahrens, and Mattheides (*Ann. Chem. Pharm.*, cxlix. 325), the hydrocarbon C_9H_{10} obtained on distilling cumic acid with calcic hydrate is not identical with normal propylbenzene; but the correctness of this conclusion is somewhat open to doubt, especially as cumic aldehyde occurs together with cymene or normal propylmethylbenzene, and as, moreover, thymol and carvacrol, and apparently also the terpenes are *normal* propyl derivatives.

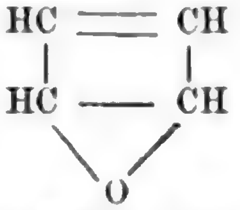
§ IV. MONALDEHYDES OF OTHER SERIES.

The only monaldehydes known besides those already described are the so called furfurol and fucusol, $C_4H_3O.COH$, cinnamic aldehyde, $C_8H_7\,COH_2$, diphenethaldehyde, $CH(C_6H_5)_2.COH$, and two isomeric naphthoic aldehydes, $C_{10}H_7.COH$.

(1662) FURFURALDEHYDE OR α-PYROMUCIC ALDEHYDE; *furfurol*: $C_5H_4O_2 = C_4H_3O.COH$.—This aldehyde is formed on heating flour, bran, sawdust, and other vegetable substances with dilute sulphuric acid or zincic chloride solution; it is also produced in small quantity on heating various kinds of wood merely with water in closed vessels, at an elevated temperature (G. Williams; Hugo Müller), and is the chief constituent of the oil which passes over with the steam on rectifying the crude product of the distillation of wood at temperatures below 200° (392° F.) (Heill, *Deut. chem. Ges. Ber.*, x. 936). According to Stenhouse, a very advantageous process for preparing it is to distil bran with more than half its weight of sulphuric acid, previously diluted with two parts of water. Schwanert, however (*Ann. Chem. Pharm.*, cxvi. 257), recommends the proportions 100 pts. sulphuric acid, 300 pts. water, and 100 pts. bran, from which he obtains 3 pts. of the aldehyde.

Furfuraldehyde is a colourless, highly refracting oil, which soon becomes coloured when kept, doubtless, however, in consequence of the presence of impurity (comp. Stenhouse, *R. Soc. Proc.*, xviii. 537); it boils at about 163° (325°·4 F.), and at 15°·6 (60° F.) has the sp. gr. 1·1648. It dissolves in about 12 pts. of cold water, but mixes with alcohol in all proportions. When boiled with water and argentic oxide, it yields the silver salt of *pyromucic acid*, $C_4H_3O\,COOH$; and the potassic salt of this acid is formed, together with *furfurylic alcohol*, $C_4H_3O.CH_2.OH$, when it is treated with an alcoholic solution of potassic hydrate (Limpricht, *Ann. Chem. Pharm.*, clxv. 300). This alcohol is more readily prepared by the action of sodium amalgam on an aqueous solution of the aldehyde maintained acid by the addition of acetic acid; on extracting the solution with ether, and distilling off the ether from the extract, it remains as a syrup; this, when exposed over sulphuric acid, gradually dries up to a colourless resin, which at once becomes green when moistened with hydrochloric acid (Baeyer, *Deut. chem. Ges. Ber.*, x. 355). Furfuraldehyde forms a crystalline compound with hydric sodic sulphite; and by the action of sulphuretted hydrogen it is converted into *thiofurfurol*, $C_4H_3O.CSH$, which is a white crystalline substance. In contact with ammonia it forms *furfuramide*, $C_{15}H_{12}N_2O_3 = 3C_5H_4O_2 + 2NH_3 - 3OH_2$, a white crystalline neutral body, insoluble in water, melting at 117° (242°·6 F.) (R. Schiff), which is at once decomposed by acids with formation of furfuraldehyde and an ammonic salt, whilst on heating it at 120° (248° F.), or by boiling with potassic hydrate solution, it is converted into the isomeric *furfurine*, a strongly basic substance. Furfurine crystallizes in white needles, which melt at 116° (240°·8 F.); it yields a number of crystalline salts, such as the hydrochloride, $C_{15}H_{13}N_2O_3Cl$. On treatment with acetic anhydride it furnishes a monacetyl derivative, $C_{15}H_{11}(C_2H_3O)N_2O_3$, which combines with 6 atoms of bromine (R. Schiff, *ibid.*, x. 1186). By the action of aniline hydrochloride and aniline on furfuraldehyde in alcoholic solution, furfuraniline hydrochloride, (?) $C_{17}H_{15}O_2N_2Cl$, is obtained, in the form of beautiful purple-coloured crystals. Furfuraldehyde is not affected by hydrochloric acid, but on adding this acid to a mixture of phenol with the aldehyde, a blue colour is produced, which becomes green on dilution with alcohol, a condensation product being formed (Baeyer). On heating furfuraldehyde with acetic anhydride and sodic acetate, &c., it is converted into *furfuracrylic* acid: $C_4H_3O.COH + CH_3.COOH = C_4H_3O.CH{=}CH.COOH + OH_2$ (Baeyer, *loc. cit.*, and *ibid.*, 695, 1358).

The most satisfactory expression of the constitution of furfuraldehyde appears to be afforded by the following formula, the arguments for the adoption of which will be discussed under pyromucic acid:



(1663) Fucusaldehyde or β-Pyromucic aldehyde; *fucusol*: $C_5H_4O_2 = C_4H_3O.COH$.—This isomeride of furfuraldehyde is formed on distillation of seaweed—*e.g.*, *Fucus nudosus*, *vesiculatus*, *serratus*, &c., with dilute sulphuric acid; and is perhaps also produced on similar treatment of some mosses and lichens (Stenhouse, *Ann. Chem. Pharm.*, xxxv. 301; lxxiv. 278; *R. Soc. Proc.*, xx. 80). Fucusaldehyde boils at about 172° (341°·6 F.); it resembles furfuraldehyde in most of its properties, but appears to be less stable. It is converted into the silver salt of *β-pyromucic acid* on boiling with water and argentic oxide, and in contact with ammonia forms *fucusamide*, $C_{15}H_{12}N_2O_3$, which by boiling with potassic hydrate solution is transformed into the isomeric *fucusine*, which is distinguished from the isomeric furfurine by crystallizing in small laminæ united in stellate groups; fucusine yields crystalline salts such as the nitrate $C_{15}H_{13}N_2O_3(NO_3)$.

(1664) Cinnamic or Phenylacrylic aldehyde: $C_6H_5.CH{=}CH.COH$ or C_9H_8O.—This aldehyde forms the greater portion of the oils of cinnamon and cassia, in which it occurs along with a small quantity of hydrocarbons (terpenes); it may readily be extracted by agitating either of the oils with a concentrated solution of sodic or potassic hydric sulphite, separating the crystalline mass, and washing it with alcohol. When this is decomposed with dilute sulphuric acid, the aldehyde separates as an oil which may be washed, dried, and distilled.

Cinnamic aldehyde is formed on oxidization of cinnamic alcohol (1483) by oxygen in presence of platinum black, and is produced synthetically when a mixture of benzaldehyde and ethaldehyde is saturated with hydrochloric acid gas: $C_6H_5.COH + CH_3.COH = C_6H_5.CH{=}CH.COH + OH_2$.

It is a colourless oil, heavier than water, and insoluble in it; it boils at about 248° (478°·4 F.), being slightly decomposed, and readily volatilizes with vapour of water. It gradually absorbs oxygen on exposure to the air, being converted into cinnamic acid; the more powerful oxidizing agents convert it into benzoic aldehyde and benzoic acid. When submitted to the action of ammonia, it yields crystalline *hydrocinnamide*, $C_{27}H_{24}N_2$. By heating it with acetic anhydride and sodic acetate and the homologous compounds, Perkin has obtained a series of acids such as *cinnamenylacrylic acid*, $C_6H_5.CH{=}CH.CH{=}CH.COOH$ (*Journ. Chem. Soc.*, 1877, i. 403).

(1665) **Diphenethaldehyde**: $CH(C_6H_5)_2.COH$, is formed together with diphenylethylenic oxide on distillation of hydrobenzoin and isohydrobenzoin with dilute sulphuric acid; it is a colourless oil, yielding diphenylketone, $CO(C_6H_5)_2$, on oxidation (Zincke, *Deut. chem. Ges. Ber.*, ix. 1769).

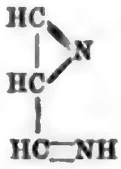
(1666) **Naphthoic aldehydes**: $C_{11}H_8O = C_{10}H_7.COH$.—When a mixture of the calcic salts of α- and β-naphthoic acids is distilled with calcic formate, a mixture of the corresponding aldehydes is obtained. The pure β-aldehyde is formed together with much naphthalene when pure β-naphthoate is employed, but the α-aldehyde cannot be prepared from the pure α-naphthoate, probably owing to the comparatively low temperature at which the salt decomposes. *α-Naphthoic aldehyde* is an oily liquid, boiling at about 280° (536° F.), but it cannot be distilled alone without decomposition. *β-Naphthoic aldehyde* crystallizes in lustrous plates, which melt at 59°·5 (139°·1 F.); it is only very slightly soluble in cold water, but readily in alcohol and ether (Battershall, *Ann. Chem. Pharm.*, clxviii. 114).

§ V. Dialdehydes.

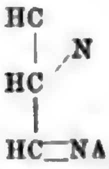
The only dialdehydes at present known are oxalic aldehyde or glyoxal, COH.COH, succinic aldehyde, $C_2H_4(COH)_2$, and the isomeric phthalic and terephthalic aldehydes, $C_6H_4(COH)_2$.

(1667) **Oxalic aldehyde**; *glyoxal*: $C_2H_2O_2 = COH.COH$.—This aldehyde bears the same relation to glycol and oxalic acid that ethaldehyde does to ethylic alcohol and acetic acid. It was discovered by Debus in 1856, when examining the products of the action of nitric acid on ethylic alcohol, being formed together with glycollic acid, $CH_2(OH).COOH$, glyoxylic acid, $CH(OH)_2.COOH$, and oxalic acid, COOH.COOH, &c. Glyoxal is obtained from the neutral liquid remaining after the separation of these acids as calcic salts (*v.* glyoxylic acid), by evaporating it to a syrup and mixing the residue with several times its volume of a concentrated solution of hydric sodic sulphite; after a time, the sides of the vessel become covered with a white crystalline crust of the compound of the aldehyde with the acid sulphite $[CH(OH).SO_3Na]_2 + OH_2$; this may be purified by dissolving it in the smallest possible quantity of boiling water, and allowing the solution to cool quickly. This compound is converted into the barium salt by mixing a concentrated solution with baric chloride solution; the barium salt is then exactly decomposed with sulphuric acid, and the filtrate from the baric sulphate evaporated to dryness. The aldehyde cannot be separated by means of sodic carbonate, as on adding this salt the liquid becomes yellowish-brown, and a dark-coloured precipitate is produced. According to Lubavin (*Deut. chem. Ges. Ber.*, viii. 768; Wyss, *ibid.*, x. 1365), it is far more advantageous to employ a mixture of equal parts of ethaldehyde and water than alcohol: 100 parts of ethaldehyde yielding from 45 to 100 of the compound of glyoxal with hydric sodic sulphite.

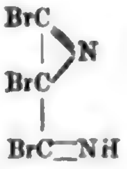
Oxalic aldehyde is a transparent, amorphous, deliquescent substance, extremely soluble in water, alcohol, and ether. It reduces an ammoniacal solution of a silver salt with great facility; a small quantity of very dilute nitric acid converts it into glyoxylic acid, $CH(OH)_2.COOH$, while by a larger quantity even of the very dilute acid it is converted into oxalic acid. Alkalies convert it even in the cold into the corresponding salt of glycolic acid, $CH_2(OH).COOH$. On passing ammonia into its ethereal solution, a white precipitate is formed, apparently consisting of the compound with ammonia, but when it is submitted to the action of strong aqueous ammonia, *glyoxaline*, $C_3H_4N_2$, and *glycosine*, $C_6H_6N_4$, are produced, the former being the chief product. Glycosine is produced merely by the separation of the elements of water: $3C_2O_2H_2 + 4NH_3 = C_6H_6N_4 + 6OH_2$, but the formation of glyoxaline is accompanied by that of formic acid: $2C_2O_2H_2 + 2NH_3 = C_3H_4N_2 + HCOOH + 2OH_2$ (Debus, *Ann. Chem. Pharm.*, cii. 20; cvii. 199; cx. 316; cxviii. 253). Glycosine is nearly insoluble in cold, sparingly soluble in hot water; it may be sublimed by careful heating, forming a bulky sublimate consisting of needle-shaped crystals; it dissolves in hydrochloric acid solution, yielding a crystalline hydrochloride; and also dissolves in sodic hydrate solution on boiling. Glyoxaline is very soluble in water, and the solution is strongly alkaline. According to Wyss (*loc. cit.*) it crystallizes in large glistening prisms, which melt at about 88° (190°·4 F.), and it boils constantly at 255° (491° F.). Its vapour density corresponds with the formula $C_3H_4N_2$. It is not acted upon by acetic chloride or anhydride, or by benzoic chloride; but when it is warmed with ethylic bromide, a single atom of hydrogen is displaced by ethyl, and the resulting compound unites with a molecule of the bromide. It is entirely decomposed by potassic permanganate, but is not affected by chromic acid; reducing agents are without action. Bromine converts it into *tribromoglyoxaline*, $C_3HBr_3N_2$, which exhibits marked acid properties, dissolving in alkaline solutions, from which it is precipitated unchanged on the addition of an acid; by the addition of salts of the heavy metals to solutions of the alkali metal derivatives, white insoluble or difficultly soluble precipitates of the corresponding metallic derivatives are produced. The silver derivative, $C_3AgBr_3N_2$, is remarkable for its stability; by digesting it with methylic or ethylic iodide, methyl- and ethyl-tribromoglyoxaline are obtained. A silver derivative of glyoxaline, $C_3AgH_3N_2$, is obtained as a white voluminous precipitate on adding argentic nitrate to its aqueous solution; and from this compound corresponding methyl and ethyl derivatives may be prepared by the action of methylic and ethylic iodides. From these observations Wyss concludes that glyoxaline and its silver and bromo-derivatives are most probably represented by the following formulæ:



Glyoxaline.



Silver glyoxaline.



Tribromoglyoxaline.

According to Schiff (*Gaz. chim. ital.*, iv. 16), when hydrochloric acid gas is passed into a solution of glyoxal in acetic acid, and the mixture is allowed to stand, it deposits a white crystalline powder very similar to potato-starch in appearance. This compound, *hydrohexaglyoxal*, $C_{12}H_{14}O_{13}$, is formed by the condensation of 6 mols. of glyoxal, and the assimilation of 1 mol. of water; it is destitute of aldehydic character, however, but appears to contain a single OH group, as it yields a monaceto-derivative when treated with acetic anhydride. It is almost insoluble in all ordinary solvents, and is a body of great stability.

(1668) **Succinic aldehyde**: $C_4H_6O_2 = CH_2(COH).CH_2(COH)$.—This aldehyde is produced by the action of sodium amalgam on a mixture of succinic chloride, acetic acid, and ether. It is liquid and soluble in water, and boils at about 202° (395°·6 F.). It forms a crystalline compound with hydric sodic sulphite; oxidizing agents convert it into succinic acid; on heating it with baric or calcic hydrate and water the corresponding salt of normal oxybutyric acid, $CH_2(OH).CH_2.CH_2.COOH$, is formed (A. Saytzeff, *Ann. Chem. Pharm.*, clxxi. 251.)

(1669) **Phthalic aldehyde**: $C_8H_6O_2 =$ (?) $C_6H_4(COH)_2$.—This aldehyde is formed when phthalic chloride is digested with zinc and dilute hydrochloric acid (Kolbe and Wischin, *Journ. Chem. Soc.*, xix. 339), or with magnesium and acetic acid (Baeyer), and is best prepared by the former method, using an ethereal solution of the chloride (Baeyer, *Deut. chem. Ges. Ber.*, x. 123; Hessert, *ibid.*, 1445). It crystallizes in small rhombic plates, melting at 65° (149° F.), only slightly soluble in cold, but more readily in hot water; it is readily oxidized to phthalic acid by an alkaline solution of potassic permanganate. Like the aldehydes generally, it forms a crystalline compound with hydric sodic sulphite. Alkalies readily transform it into phthalaldehydic acid, $C_8H_6O_3$, which on mere boiling with water is reconverted into the aldehyde. By the action of sodium amalgam on its alcoholic solution, a crystalline compound of the formula $C_{16}H_{18}O_4 = C_6H_4(CH_2.OH).CH(OH).CH(OH).C_6H_4(CH_2.OH)$ is produced, together with a non-crystalline body which perhaps is the compound $C_6H_4(COH).CH_2.OH$.

(1670) **Terephthalic aldehyde**: $C_8H_6O_2 = C_6H_4(COH)_2(COH : COH = 1:4$.—According to Grimaux (*Compt. Rend.*, lxxxiii. 825), this aldehyde is formed on heating the dichloroparaxylene of the formula $C_6H_4(CH_2Cl)_2$ with plumbic oxide and water. It crystallizes in long, slender, colourless needles, which melt at about 114° (237°·2 F.).

CHAPTER IX.

THE KETONES.

§ I. *Ketones of the* $CO(C_nH_{2n+1})_2$ *Series*;—§ II. *Ketones of the* $C_nH_{2n+1}.CO.C_nH_{2n-7}$ *and* $CO(C_nH_{2n-7})_2$ *Series*;—§ III. *Ketones of other Series. Camphor*;—§ IV. *Quinones*;—§ V. *Sulphines and Sulphones.*

The ketones are closely related in their properties to the aldehydes, and may be regarded as derived from them by the displacement of the hydrogen of the group COH characteristic of the aldehydes by hydrocarbon radicles; they may also be regarded as compounds of carbonic monoxide with hydrocarbon radicles, or as formed by the displacement of the OH groups in carbonic acid, $CO(OH)_2$, by hydrocarbon radicles; and they bear a similar relation to the secondary monohydric carbinols that the aldehydes do to the primary monohydric carbinols, being formed from them on oxidation in precisely the same manner as the aldehydes are from the primary carbinols; thus:

$$\underset{\text{Primary carbinol.}}{R'.CH_2(OH)} \qquad \underset{\text{Aldehyde.}}{R'.COH} \qquad \underset{\text{Secondary carbinol.}}{R'_2.CH(OH)} \qquad \underset{\text{Ketone.}}{R'_2.CO}$$

With few exceptions, the ketones at present known all correspond to the general formula COR'_2: that is to say, they consist of only monad radicles associated with the group CO.

(1671) *Formation.*—1. By oxidation of the secondary monohydric carbinols, which may be represented as occurring in the following manner:

$$\begin{aligned} R'_2.CH(OH) + (O+OH_2) &= R'_2.C(OH)_2 + OH_2; \\ R'_2.C(OH)_2 &= R'_2.CO + OH_2. \\ \underset{\text{Dimethyl carbinol.}}{(CH_3)_2.CH(OH)} + (O+OH_2) &= (CH_3)_2.C(OH)_2 + OH_2; \\ (CH_3)_2.C(OH)_2 &= \underset{\text{Dimethyl ketone.}}{(CH_3)_2.CO} + OH_2. \end{aligned}$$

2. By distillation of the metallic salts of the acids, and particularly of the baric or calcic salts, either alone or mixed with that of another acid, this method being more especially applicable to the preparation either of ketones containing only radicles of the C_nH_{2n+1} series, or a radicle of that series in association with an isologous radicle; the reaction is precisely analogous to that which takes place in the formation of aldehydes by distillation of the salts of acids with a formate, the group OH of the COOH group in the acid becoming in the one case displaced by hydrogen, and in the other by a hydrocarbon radicle:

$$\underset{\text{Calcic salt of acid.}}{(R'.COO)_2Ca} = \underset{\text{Simple ketone.}}{R'_2.CO} + CaCO_3.$$

$$\underset{\text{Calcic acetate.}}{(CH_3.COO)_2Ca} = \underset{\text{Dimethyl ketone.}}{(CH_3)_2.CO} + CaCO_3.$$

$$\underset{\text{Calcic salt of acid.}}{(R'.COO)_2Ca} + \underset{\substack{\text{Calcic salt of isomeric,} \\ \text{homologous or isologous acid.}}}{(R'.COO)_2Ca} = \underset{\text{Mixed ketone.}}{2R'.CO.R'} + 2CaCO_3.$$

$$\underset{\text{Calcic benzoate.}}{(C_6H_5.COO)_2Ca} + \underset{\text{Calcic acetate.}}{(CH_3.COO)_2Ca} = \underset{\text{Phenylmethyl ketone.}}{2C_6H_5.CO.CH_3} + 2CaCO_3.$$

3. By the action of the zinc organo-metallic compounds on acid chlorides, the product being at once treated with water. This method has hitherto only been applied to the preparation of simple and mixed ketones of the $(C_nH_{2n+1})_2CO$ series, and of mixed ketones containing a radicle of the C_nH_{2n+1} series in association with an isologous radicle.

According to Pawlow's recent experiments (*Ann. Chem. Pharm.*, clxxxviii. 104), the reaction takes place in the manner suggested by Wagner and Saytzeff (*comp.* p. 412), thus:

$$R'.COCl + Zn(C_nH_{2n+1})_2 = R'.C(C_nH_{2n+1})(O.ZnC_nH_{2n+1})Cl,$$

the product at this stage being decomposed on treatment with water in accordance with the following equations:

$$R'.C(C_nH_{2n+1})(O.ZnC_nH_{2n+1})Cl + 2OH_2 =$$
$$R'.C(C_nH_{2n+1})(OH)Cl + Zn(OH)_2 + C_nH_{2n+2};$$
$$R'.C(C_nH_{2n+1})(OH)Cl = R'.CO.C_nH_{2n+1} + HCl.$$

But the product of the first action may be directly converted into the ketone by the action of a further quantity of the acid chloride (Pawlow):

$$R'.C(C_nH_{2n+1})(O.ZnC_nH_{2n+1})Cl + R'COCl = 2R'.CO.C_nH_{2n+1} + ZnCl_2,$$

so that the amounts of acid chloride and zinc organo-metallic compound required for the formation of the ketone would appear to be in the proportion of $2R'.COCl : Zn(C_nH_{2n+1})_2$; Pawlow finds, however, that it is often advantageous to employ an excess of the zinc compound, especially in the preparation of ketones containing tertiary radicles of the form $C(C_nH_{2n+1})_3$ (*pinacolins*), the most favourable proportions being about 1 mol. R.'COCl to 1½ mols. $Zn(C_nH_{2n+1})_2$.

4. By the action of carbonic monoxide on the sodium organo-metallic compounds (Wanklyn); as only the radicles of the C_nH_{2n+1} series are known to combine with sodium, this method is restricted to the formation of ketones of the $CO(C_nH_{2n+1})_2$ series:

$$CO + 2NaC_nH_{2n+1} = CO(C_nH_{2n+1})_2 + 2Na.$$
$$CO + \underset{\text{Sodic ethide.}}{2NaC_2H_5} = \underset{\text{Diethyl ketone.}}{CO(C_2H_5)_2} + 2Na.$$

5. By the action of acid chlorides on hydrocarbons in presence of aluminic chloride (Friedel and Crafts, *Compt. Rend.*, lxxxiv. 1392, 1450; lxxxv. 74); for example:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Bezoic chloride.}}{C_6H_5.COCl} = \underset{\text{Diphenyl ketone.}}{C_6H_5.CO.C_6H_5} + HCl.$$

Other chlorides, such as zincic and ferric chloride, exert a similar influence, and not only organic acid chlorides, but also the chlorinated as well as brominated and iodated derivatives of hydrocarbons having the halogen associated with carbon atoms forming part of an "open chain" in like manner enter readily into reaction with hydrocarbons, considerable heat being developed in most cases. Thus on passing methylic chloride into a warm solution of aluminic chloride in benzene, mono-, di-, tri-, and even tetramethylated benzenes are formed; similarly, benzylic chloride and benzene yield di- and triphenylmethane, as well as other products not yet investigated; and by the action of aluminic chloride on a mixture of benzene and tetrachloromethane, tetraphenylmethane, $C(C_6H_5)_4$, is produced. Chlorobenzene, however, is entirely without action on benzene in presence of aluminic chloride. The manner in which the metallic chlorides act is at present obscure, however; Friedel and Crafts suppose that an aluminic compound is first formed by the action of the aluminic chloride on the hydrocarbon, which then enters into reaction with the haloid organic compound, aluminic chloride being regenerated; thus:

$$C_6H_6 + Al_2Cl_6 = C_6H_5.Al_2Cl_5 + HCl;$$
$$C_6H_5.Al_2Cl_5 + C_6H_5.CH_2Cl = C_6H_5.CH_2.C_6H_5 + Al_2Cl_6.$$

The discovery of this property of certain metallic chlorides of inducing, as it were, the formation of haloid acid is of much interest, and serves to throw light on the production of hydrocarbons by Zincke's method (*vid.* p. 359), and of a complex mixture of olefines and paraffins on distilling fermentation amylic alcohol with zincic chloride (p. 194).

6. By heating acids of the benzoic and naphthoic series with hydrocarbons such as benzene and naphthalene and phosphoric anhydride, whereby under the dehydrating influence of the anhydride the OH of the COOH group of the acid becomes separated together with an atom of hydrogen from the hydrocarbon; thus:

$$C_6H_6 + C_6H_5.COOH + P_2O_5 = (C_6H_5)_2CO + 2HPO_3.$$

7. By oxidation of the acids of the lactic series, and of other oxy-acids of the general formula $R'_2C(OH).COOH$; for example:

$$\underset{\text{Oxyisobutyric acid.}}{(CH_3)_2C(OH).COOH} + (O + OH_2) = (CH_3)_2C(OH)_2 + H_2CO_3;$$

$$(CH_3)_2C(OH)_2 = \underset{\text{Dimethyl ketone.}}{(CH_3)_2CO} + OH_2.$$

8. By the action of alkalies on ethylic acetoacetate and allied compounds; thus:

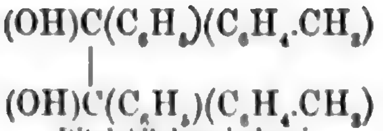
$$\underset{\text{Ethylic acetoacetate.}}{CH_3.CO.CH_2.COOC_2H_5} + Ba(OH)_2 = \underset{\text{Dimethyl ketone.}}{CH_3.CO.CH_3} + BaCO_3 + C_2H_5.OH.$$

This method is perhaps one of the most generally available for the preparation of ketones. Ethylic acetoacetate is a product of the action of sodium on ethylic acetate (q. v.); when treated with sodium, it yields a monosodium derivative, $CH_3.CO.CHNa.COOC_2H_5$, from which by the action of monohaloid hydrocarbon derivatives a variety of compounds of the form $CH_3.CO.CHR'.COOC_2H_5$ may be obtained, which all yield ketones of the form $CH_3.CO.CH_2R'$ on decomposition with alkali; and by the action of sodium and then of monohaloid hydrocarbon derivatives on these compounds, a series of bodies of the form $CH_3.CO.CR'\mathit{R'}.COOC_2H_5$ are produced, which also furnish corresponding ketones $CH_3.CO.CHR'\mathit{R'}$. Ethylic propionate may in a similar manner be converted into the compound $CH_3.CH_2.CO.CH_2.CH_2.COOC_2H_5$ (Hellon and Oppenheim), from which doubtless a series of ethylated ketones are derivable.

9. By distillation of the glycols formed by hydrogenation of the ketones with sulphuric acid; for example:

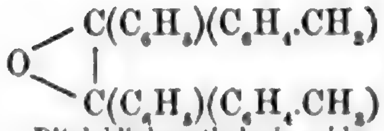
$$\underset{\text{Tetramethyl glycol (pinacone).}}{(CH_3)_2C(OH).C(CH_3)_2.OH} - OH_2 = \underset{\text{Methyl tertiary-butyl ketone (pinacolin).}}{CH_3.CO.C(CH_{33})}.$$

The formation of ketones in this manner, however, is obviously the result of isomeric change, and it is only quite recently that some light has been thrown on the manner in which this takes place by the experiments of Thörner and Zincke (*Deut. chem. Ges. Ber.*, ix. 1738, 1761). According to Thörner, two isomeric compounds are formed simultaneously from diparatolyl-diphenyl ketone, one being a derivative of ethylenic oxide and the other a ketone, and of these the former is readily converted into the latter by merely warming with benzoic chloride or heating with acids; thus:

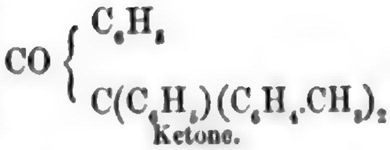


$$\begin{array}{l}(OH)C(C_6H_5)(C_6H_4.CH_3)\\ \quad | \\ (OH)C(C_6H_5)(C_6H_4.CH_3)\end{array}$$

Ditolyldiphenyl glycol.



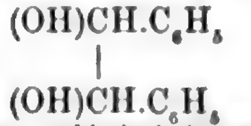
Ditolyldiphenethylenic oxide.



$$CO\left\{\begin{array}{l}C_6H_5\\ C(C_6H_5)(C_6H_4.CH_3)_2\end{array}\right.$$

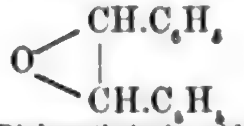
Ketone.

The glycols formed by hydrogenation of the aldehydes apparently exhibit a similar behaviour, as the so-called hydrobenzoin and isohydrobenzoin yield both an ethylenic oxide derivative and an aldehyde (Zincke); thus:

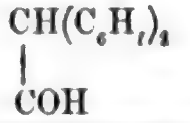


$$\begin{array}{l}(OH)CH.C_6H_5\\ \quad | \\ (OH)CH.C_6H_5\end{array}$$

Hydro- and isohydrobenzoin.



Diphenethylenic oxide.



$$\begin{array}{l}CH(C_6H_5)_2\\ | \\ COH\end{array}$$

Diphenethaldehyde.

The formation of derivatives of ethylenic oxide in this manner is perfectly normal, being analogous to that of ethylenic oxide itself from glycol; their conversion either into an aldehyde or a ketone is the consequence of the transference of the hydrocarbon radicle to a contiguous carbon atom, so to speak, in exchange for oxygen, and is a further illustration of the accumulation of hydrocarbon radicles leading to the production of more stable compounds, of which several instances have been previously described (pp. 399, 442).

10. By heating dihaloid hydrocarbon derivatives of the form CCl_2R_2 with water; for example:

$$\underset{\text{Diphenyldichloromethane.}}{CCl_2(C_6H_5)_2} + OH_2 = \underset{\text{Diphenyl ketone.}}{CO(C_6H_5)_2} + 2HCl.$$

11. Ketones, and especially dimethyl ketone or acetone, are often obtained as products of the dry distillation of complex highly oxygenated bodies such as sugar, and of wood.

(1672) *Properties.*—1. The majority of the ketones are volatile liquids, difficultly soluble or insoluble in water; they are much more stable, and less liable to change and to enter into reaction with other bodies than the aldehydes, and especially do not exhibit the tendency to polymerize which is so characteristic of many of the latter; they also oxidize much less readily, being without action on an ammoniacal solution of a silver salt.

2. When submitted to the action of nascent hydrogen, they yield a mixture of a monohydric secondary carbinol, and of a dihydric alcohol (so-called pinacone):

$$R'_2.CO + HH = R'_2.CH(OH)\,;\; 2R'_2.CO + HH = \begin{array}{l}R'_2.C(OH)\\ \quad\;\; | \\ R'_2.C(OH)\end{array}.$$

$$\underset{\text{Dimethyl ketone.}}{CH_3.CO.CH_3} + HH = \underset{\text{Dimethyl carbinol.}}{CH_3.CH(OH).CH_3}.$$

$$\underset{\text{Dimethyl ketone.}}{2(CH_3)_2.CO} + HH = \underset{\text{Tetramethyl glycol.}}{(CH_3)_2C(OH).C(OH)(CH_3)_2}.$$

The proportion in which the two compounds are formed depends much on the conditions of experiment. According to Friedel, if an aqueous solution of acetone be treated with sodium amalgam, isopropylic alcohol is almost exclusively produced, but if the amount of ketone dissolved be diminished by adding potassic carbonate to the water, the glycol is the chief product.

3. The ketones do not furnish corresponding acids on oxidation, but are decomposed into products containing fewer carbon atoms; it has been shown, chiefly by Popoff, that one of the hydrocarbon groups always remains in combination with the CO group, and forms by assumption of OH the corresponding acid, whilst the other is split off and separately oxidized. For example:

$$\underset{\text{Methylpropyl ketone.}}{CH_3.CO.CH_2.CH_2.CH_3} + 3(O + OH_2) = \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Propionic acid.}}{CH_3.CH_2.COOH} + 3OH_2.$$

$$\underset{\text{Methylphenyl ketone.}}{C_6H_5.CO.CH_3} + 3(O + OH_2) = \underset{\text{Benzoic acid.}}{C_6H_5.COOH} + \underset{\text{Formic acid.}}{HCOOH} + 3OH_2.$$

Apparently it is always the less stable radicle which is thus split off, and the product or products of the oxidation of this radicle are identical with those obtained on oxidation of the corresponding alcohol: it may, in fact, be supposed that the ketones are in the first instance resolved into an acid and an alcohol on oxidation in the manner shown by the general equation:

$$\underset{\text{Ketone.}}{R'.CO.R'} + (O + OH_2) = \underset{\text{Acid.}}{R'.COOH} + \underset{\text{Alcohol.}}{R'.OH};$$

the alcohol being then at once further oxidized.

If both radicles are of the same type—that is to say, if both are normal or iso-primary, secondary or tertiary—but contain a different number of carbon atoms, the radicle which is split off is always that which contains the greater number of carbon atoms. From ketones containing radicles of different types, however, if they belong to the $CO(C_nH_{2n+1})_2$ series and contain a normal and iso-primary radicle, the iso-primary is removed; while from those containing a normal or iso-primary associated with a normal or iso-secondary radicle, the normal or iso-secondary radicle is split off; and those which contain a normal and an iso-secondary radicle lose the latter. The behaviour of ketones of this series containing identical, isomeric or homologous normal primary or isoprimary radicles, may therefore be briefly expressed by the general equation:

$$\underset{\text{Normal or iso-primary ketone.}}{C_nH_{2n+1}.CH_2.CO.CH_2.C_mH_{2m+1}} + 3(O + OH_2) =$$
$$\underset{\text{Primary acid.}}{C_nH_{2n+1}.CH_2.COOH} + \underset{\text{Acid.}}{C_mH_{2m+1}.COOH} + 3OH_2.$$

where *n* and *m* may have the same or different values, the nature of the acid or acids obtained depending, of course, on the nature of the radicles.

The behaviour of ketones containing identical, isomeric or homologous normal secondary or isosecondary radicles, may in a similar manner be exhibited by the equation:

$$\underset{\text{Normal or iso-secondary ketone.}}{(C_nH_{2n+1})_2CH.CO.CH(C_mH_{2m+1})_2} + 2(O + OH_2) =$$
$$\underset{\text{Secondary acid.}}{(C_nH_{2n+1})_2CH.COOH} + \underset{\text{Ketone.}}{CO(C_mH_{2m+1})_2} + 2OH_2;$$

whilst the following expression indicates the nature of the oxidation products of ketones containing a normal primary or isoprimary radicle associated with a normal secondary or isosecondary radicle:

$$\underset{\text{Normal or iso-primary normal or iso-secondary ketone.}}{C_nH_{2n+1}.CH_2.CO.CH(C_mH_{2m+1})_2} + (O + OH_2) =$$
$$\underset{\text{Primary acid.}}{C_nH_{2n+1}.CH_2.COOH} + \underset{\text{Ketone.}}{CO(C_mH_{2m+1})_2} + OH_2.$$

The ketones containing tertiary radicles of the C_nH_{2n+1} series associated with normal primary radicles of the same series, which are almost the only ketones with tertiary radicles that have been prepared, behave somewhat differently, as the tertiary radicle remains in combination with the CO group, the primary radicle being split off and separately oxidized, so that their behaviour may be represented by the equation:

$$C(C_nH_{2n+1})_3.CO.CH_2.C_mH_{2m+1} + 3(O+OH_2) =$$

Primary tertiary ketone.

$$C(C_nH_{2n+1})_3.COOH + C_mH_{2m+1}COOH + 3OH_2.$$

Tertiary acid. Acid.

These ketones, in fact, closely resemble those containing radicles such as phenyl —*i.e.*, in which the CO group is associated with a carbon atom forming part of a closed chain—together with a radicle of the C_nH_{2n+1} series, from which the latter is always split off and separately oxidized; thus:

$$C_6H_5.CO.C_2H_5 + 3(O+OH_2) = C_6H_5COOH + CH_3.COOH + 3OH_2.$$

Ethylphenyl ketone. Benzoic acid. Acetic acid.

In those cases in which the methyl group is split off, instead of formic acid, which is the normal oxidation product of this group, carbonic anhydride and water are obtained, owing to the further oxidation of the acid; the lower ketones formed as the first products of oxidation of the ketones containing secondary radicles also very readily undergo further oxidation at the moment of formation.

The behaviour of several of the ketones of the $CO(C_nH_{2n+1})_2$ series, when oxidized by concentrated nitric acid, is somewhat peculiar, substances being produced which apparently are mono-nitro-derivatives of acids of the acetic series. Thus, dipropyl ketone yields a body of the composition of nitropropionic acid, $C_2H_4(NO_2).COOH$, and dibutyl and dipentyl ketones furnish compounds bearing to them a similar relation in composition (comp. Schmidt, *Deut. chem. Ges. Ber.*, v. 599).

4. Certain of the ketones form crystalline compounds with the acid sulphites analogous to those furnished by the aldehydes, but this property is only common to those which contain the group CH_3 associated either with a primary or secondary radicle of the C_nH_{2n+1} series, and to those in which the CO group is not associated with a carbon atom forming part of a closed chain; those which contain the CH_3 group and a tertiary radicle of the C_nH_{2n+1} series or a radicle such as phenyl, tertiary-butylmethyl ketone or pinacolin, $C(CH_3)_3.CO.CH_3$, and phenylmethyl ketone, $C_6H_5.CO.CH_3$, for example, do not form such compounds.

5. Dimethyl ketone or acetone unites with hydrocyanic acid, forming an exceedingly unstable cyano-derivative, which on digestion with hydrochloric acid solution is converted into oxyisobutyric acid:

$$CH_3.CO.CH_3 + HCN = (CH_3)_2C(OH).CN;$$

Dimethyl ketone. Cyanodimethyl carbinol.

$$(CH_3)_2C(OH).CN + 2OH_2 + HCl = (CH_3)_2C(OH).COOH + NH_4Cl.$$

Cyanisopropylic alcohol. Oxyisobutyric acid.

It has not been ascertained, however, whether this property is common to all the ketones; probably it is not.

6. Crystalline compounds with ammonia analogous to those furnished by the aldehydes have not been obtained from the ketones, but many of them appear to enter into reaction with ammonia somewhat after the manner of the aldehydes, forming more or less complex basic compounds with separation of the elements of water (comp. p. 780). Amines, such as aniline, which are violently acted upon by the aldehydes, are unaffected by the ketones; and they are not known either to combine or to form condensation compounds with the acid amides, such as are readily yielded by the aldehydes. By the action of ammonia and sulphuretted hydrogen, and of ammonia and carbonic bisulphide respectively on dimethyl ketone, crystalline compounds are formed, which apparently are the analogues of thialdin and carbothialdin (p. 739), but this property has not been observed of other ketones.

7. By the action of phosphoric pentachloride on ketones, the oxygen is displaced by the equivalent amount of chlorine:

$$\underset{\text{Dimethyl ketone.}}{CH_3.CO.CH_3} + PCl_5 = \underset{\beta\text{-Dichloropropane.}}{CH_3.CCl_2.CH_3} + POCl_3.$$

The pentabromide has a similar action in many cases, and in others acts as a brominating agent.

8. When submitted to the action of chlorine or bromine, they furnish haloid substitution derivatives. Dimethyl ketone forms an unstable additive compound with bromine, but this has not been observed to take place with other ketones.

9. Their behaviour when heated with alkalies is somewhat similar to that on oxidation, one of the hydrocarbon radicles being split off in combination with hydrogen, and displaced by the residue OM′ of the metallic hydroxide HOM′, so that a hydrocarbon and a metallic salt are produced; thus:

$$\underset{\text{Diphenyl ketone.}}{C_6H_5.CO.C_6H_5} + HOK = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Benzoic acid.}}{C_6H_5.COOK}.$$

Probably the radicle which is split off is the same as is removed and separately oxidized on treatment with oxidizing agents.

10. The ketones undergo condensation under the influence of various reagents, especially hydrochloric and sulphuric acid, although much less readily than the aldehydes.

The changes are apparently of a precisely similar character to those which result in the formation of condensation products of the aldehydes (comp. p. 717). Thus when acetone is saturated with gaseous hydrochloric acid, and the solution allowed to stand for some days, two ketones resulting from the condensation of two and three molecules respectively of acetone are produced, termed mesityloxide, $C_6H_{10}O$, and phorone, $C_9H_{14}O$; the formation of the former may be represented in the following manner:

$$CH_3.CO.CH_3 + HCl = CH_3.CCl(OH).CH_3;$$
$$CH_3.CCl(OH).CH_3 + CH_3.CO.CH_3 = (CH_3)_2C{=}CH.CO.CH_3 + OH_2 + HCl;$$

and the latter may be regarded as formed in a precisely similar manner from the former and acetone. Again, when acetone is carefully distilled with concentrated sulphuric acid, mesityloxide and the modification of trimethylbenzene known as mesitylene are obtained, this hydrocarbon being probably the product of the interaction of several molecules of the compound formed by the union of the acetone with the acid; thus:

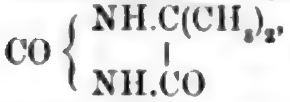
$$CH_3.CO.CH_3 + H_2SO_4 = CH_3.C(OH)(HSO_4).CH_3;$$
$$3CH_3.C(OH)(HSO_4).CH_3 = C_6H_3(CH_3)_3 + 3OH_2 + 3H_2SO_4.$$

Condensation products are also obtained by the action of sodium, calcic oxide, zincic chloride, the zinc organo-metallic compounds, &c.; and by acting on mixtures of ketones with hydrochloric and sulphuric acids, &c., compounds homologous with mesityloxide and with mesitylene may be produced. Apparently the condensation of the ketones requires the presence of a very much larger amount of the condensing agent than suffices to induce similar changes in the case of the aldehydes. Thus, if methylphenyl ketone, $CH_3.CO.C_6H_5$, be merely saturated with hydrochloric acid gas, no change takes place, but if it be supersaturated, and the mixture allowed to stand, the hydrocarbon triphenylbenzene, $C_6H_3(C_6H_5)_3$, is produced in considerable quantity (Heyne): the separation of the elements of water from several molecules of the compound $C_6H_5.CCl(OH).CH_3$, formed by the union of the ketone and acid, would appear therefore to take place only under the dehydrating influence of the excess of acid.

§ I. KETONES OF THE $(C_nH_{2n+1})_2CO$ SERIES.

(1673) **DIMETHYL KETONE OR ACETONE**: $C_3H_6O{=}CH_3.CO.CH_3$.—This ketone is formed:—1. By the oxidation of isopropylic alcohol. 2. By the dry distillation of acetates. Baric acetate yields a pure product; calcic acetate requires a higher temperature to decompose it, and in consequence a part of the acetone undergoes change; this salt, however, is most conveniently employed for the preparation of acetone. According to Fittig (*Ann. Chem. Pharm.*, cx. 17), the crude product of the distillation of acetates contains, besides acetone, ethyl- and propylmethyl ketones and dumasin, $C_6H_{10}O$, an isomeride of mesityloxide. 3. By the action of zincic methide on acetic chloride. 4. By oxidation of oxyisobutyric acid, $(CH_3)_2C(OH).COOH$. 5. By the decomposition of ethylic acetoacetate, $CH_3.CO.CH_2.COOC_2H_5$, with baryta water. 6. By the action of water at about 200° (392° F.) on δ-dichloropropane, $CH_3.CCl_2.CH_3$, and δ-dibromopropane; on β-dichloropropane, $CH_3.CHCl.CH_2Cl$, and β-dibromopropane, (the former yielding at the same time a certain quantity of the isomeric propaldehyde,* $CH_3.CH_2.COH$,) and on chloropropylene, $CH_3.CCl{=}CH_2$, and bromopropylene (Linnemann, *ibid.*, clxi. 58—70). 7. Together with other products, by the decomposition of acetic acid at high temperatures, and by the dry distillation of tartaric and citric acids, carbohydrates, and wood; hence it occurs in crude wood spirit. It has been found in the urine in cases of diabetes (Markownikoff, *ibid.*, clxxxii. 362).

Dimethyl ketone is a mobile colourless liquid, of peculiar pleasant odour, miscible in all proportions with water, alcohol, and ether; it boils at 56° (132°·8 F.) and at 0° has the sp. gr. ·814. Like alcohol, it dissolves a large number of substances insoluble in water. It readily unites with acid sulphites, forming sulpho-salts as $2[(CH_3)_2C(OH).SO_3K] + OH_2$, which crystallizes in glistening scales, moderately soluble in water; the corresponding sodium and ammonium salts are anhydrous; the ketone is readily liberated from these compounds by treatment with sodic carbonate. By the action of nascent hydrogen, dimethyl ketone is converted into dimethylcarbinol and tetramethylglycol or pinacone (comp. p. 774). When oxidized either by the ordinary chromic acid mixture, or chromic acid, by a neutral, alkaline or acid solution of potassic permanganate, or by bromine and argentic oxide, it yields acetic acid and carbonic anhydride (Hercz, *Deut. chem. Ges. Ber.*, viii. 1021), scarcely any formic acid being obtained as it is for the most part further oxidized. Phosphoric pentachloride converts acetone into δ-dichloropropane, dimethyldichloromethane or methylchloracetol, $CH_3.CCl_2.CH_3$, and the corresponding dibromopropane is obtained by the action of the pentabromide. It is violently acted upon by phosphoric trisulphide; on distilling the product and fractionating the distillate, the so-called *duplothiacetone*, $C_6H_{12}S_2$, is obtained as a liquid boiling at 183°—188° (361°·4—370°·4 F.) (Wislicenus, *Zeits. Chem.* [2], v. 324).

When gaseous anhydrous hydrocyanic acid is passed into cooled acetone, much heat is developed, and a liquid product is obtained, which distils for the most part at about 120° (248° F.), consisting of the cyanide $CH_3.C(OH)(CN).CH_3$; this compound is very unstable, acetone being liberated, and a precipitate of argentic cyanide produced on mixing it with argentic nitrate solution; when digested with hydrochloric acid, it yields oxyisobutyric or acetonic acid, $(CH_3)_2C(OH).COOH$. If, however, slightly moist pure potassic cyanide is covered with acetone, and hydrochloric acid is added in the proportion of only one molecule for each molecule of cyanide present, a crystalline substance, which may be represented by the formula $(CH_3)_2C(OH).O.C(CH_3)_2(CN) = 2(CH_3)_2.C(OH).CN - OH_2$ is produced; when digested with hydrochloric acid, this compound yields both acetone and acetonic acid. Lastly, if a mixture of acetone, potassic cyanide, and potassic cyanate is similarly treated, *acetonylurea*,  $CO\left\{\begin{array}{l}NH.C(CH_3)_2,\\ \quad | \\ NH.CO\end{array}\right.$ is obtained, being formed by the conjunction of single molecules of acetone, hydrocyanic acid, and cyanic acid; when heated with hydrochloric acid at about 150° (302° F.), this compound yields amidoisobutyric acid, $(CH_3)_2C(NH_2).COOH$ (Urech, *Ann. Chem. Pharm.*, clxiv. 255.)

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* It may be supposed that the dichloropropane is first decomposed with simultaneous formation of the two chloropropylenes, $CH_3.CH{=}CHCl$ and $CH_3.CCl{=}CH_2$; and that these enter into reaction with water at the moment of formation: the one yielding propaldehyde: $CH_3.CH{=}CHCl + OH_2 = CH_3.CH_2.CHCl(OH) = HCl + CH_3.CH_2.COH$; the other acetone: $CH_3.CCl{=}CH_2 + OH_2 = CH_3.CCl(OH).CH_3 = HCl + CH_3.CO.CH_3$.

According to Heintz (*ibid.*, clxxiv. 133; clxxviii. 305, 326; clxxxiii, 276, 283, 290; clxxxv. 1; clxxxvii. 233), acetone yields a series of basic substances when submitted to the action of ammonia; the first product is *diacetonamine*, $C_6H_{13}NO_2$, which is best prepared by passing ammonia gas and acetone vapour through a Liebig's condenser heated to 100° (212° F.); on boiling this compound with acetone, or submitting acetone to the more prolonged action of ammonia, *triacetonamine*, $C_9H_{17}NO$, together with small quantities of an isomeric base, and of *dehydrotriacetonamine*, $C_9H_{15}N$, are obtained. Diacetonamine is a colourless, strongly alkaline liquid, of peculiar ammoniacal odour, which decomposes partially on distillation; it yields crystalline salts with several acids. Most probably it has the formula $CH_3.CO.CH_2.C(CH_3)_2.NH_2$. When acted upon by nitrous acid, it yields mesityloxide and *diacetone alcohol*, $CH_3.CO.CH_2.C(CH_3)_2.OH$, a colourless, syrupy liquid, boiling constantly at 164° (327°·2 F.), which is perhaps the oxygen analogue of the so-called duplothiacetone mentioned above; and when submitted to the action of nascent hydrogen, it forms *diacetonalkamine*, (?) $CH_3.CH(OH) CH_2.C(CH_3)_2.NH_2$, a monacid base boiling at 175° (347° F.). Triacetonamine crystallizes in long needles or quadratic plates, which melt at 39°·6 (103°·3 F.), and decompose at higher temperatures; on hydrogenation it yields *triacetonalkamine*, $C_9H_{17}NO$, which crystallizes in octahedra, melting at 128°·5 (262°·4 F.); nitrous acid converts it into *nitrosotriacetonamine*, $C_9H_{16}(NO)NO$, proving that it is an *imido*-compound.

Dimethyl ketone has been shown by Reynolds (*Proc. Roy. Soc.*, 1871, xix. 431) to combine with mercuric oxide, a property which its homologues appear to share with it; the resulting compounds belong to the class of colloid bodies, and exhibit somewhat remarkable properties. To obtain the compound of acetone, solutions of 40 grams $HgCl_2$ in about 500 c.c. of water, and of 29 grams KHO in about 300 c.c. of water, are prepared. About 150 c.c. of the alkali are added to a solution of 15—20 c.c. of acetone in 250 c.c. of water, and then about 250 c.c. of the mercuric chloride solution; the precipitated mercuric oxide is at first only slowly redissolved, if the liquid be not warmed; but after a time it quickly redissolves if the mixture be briskly agitated. When the first half of the mercuric chloride solution has been added, the remaining 150 c.c. of alkali are cautiously poured in, and then mercuric chloride is added until a white precipitate makes its appearance. The filtered liquid is now dialysed to remove the excess of alkali and the potassic chloride, the diffusate being frequently replaced by pure water, and the process terminated when the diffusate no longer contains chloride. The solution thus obtained is neutral to test paper; if containing 5 per cent. of the anhydrous compound, it will, if pure, remain liquid for 12—14 days, but after that time sets to a jelly, and pectisation may be brought about in a few seconds by heating it to 50° (122° F.), or by the addition of very minute quantities of hydrochloric, acetic, nitric, and many other acids, of the alkaline hydrates, and of many neutral salts. The substance which separates, after drying first in vacuo and then at 100° (212° F.), has the composition $[(CH_3)_2CO]_2Hg_3O_2$, but probably the solution contains the very unstable hydrate of this body; moreover, this hydrate exhibits distinctly marked although extrêmely feeble acid characters; Reynolds, in fact, has been led from his experiments to regard it as a tetrabasic acid. Sodic, baric, and even calcic hydrate may be used in place of potassic hydrate; it is noteworthy also, that the precipitate caused by acetic acid in a solution of the "potassium derivate" is soluble in excess of potassic hydrate *immediately after its formation*, but that it soon loses this property. Reynolds states that acetone may be detected with facility by means of this compound (*loc. cit.*, p. 440). Some at least of the homologues of dimethyl ketone behave similarly with mercuric oxide.

(1674). HALOID DERIVATIVES OF DIMETHYL KETONE.—Chlorine is readily absorbed by acetone at ordinary temperatures, *monochloracetone*, $CH_3.CO.CH_2Cl$, and *β-dichloracetone*, $CH_3.CO.CHCl_2$, being formed according to the proportion of chlorine used (comp. Bischoff, *Deut. chem. Ges. Ber.*, v 863; viii. 1329; Mulder, *ibid.*, 1007; Theegarten, *ibid.*, vi. 897); the product is contaminated, however, with other substances resulting from the action of the chlorine on the condensation products generated by the action of the hydrochloric acid on the acetone, two of which of the composition (?) $C_5H_2Cl_3O$ and $C_6H_7Cl_3O$ have been isolated by Grabowski (*ibid.*, viii. 1438). Monochloracetone is also formed by the action of hypochlorous acid on acetone (Mulder); and by the action of sulphuric acid on the dichloropropylene $CH_2Cl.CCl{=\!=}CH_2$ (Henry, *ibid.*, v. 986). It is a colourless liquid, difficultly soluble in water, boiling at about 119° (246°·2 F.), which does not combine with acid sulphites. On treatment with argentic oxide and water, it yields acetic, glycolic, and formic acids (Linnemann). Hydrocyanic acid combines with it, forming the cyanide $CH_3.C(OH)(CN).CH_2Cl$, which on digestion with hydrochloric acid is converted into monochloroxyisobutyric acid (monochloracetonic acid), $CH_3.C(CH_2Cl)(OH).COOH$ (Bischoff). It readily enters into reaction with potassic acetate, forming the acetate $CH_3.CO.CH_2(C_2H_3O_2)$ (Henry); and with potassic iodide, potassic cyanide, and the normal sulphites (Glutz, *Journ. pr. Chem.* [2], i. 141). Concentrated nitric acid converts it into a crystalline body of the formula $C_3H_4ClNO_2$ (Glutz, Barbaglia, *Deut. chem. Ges. Ber.*, vi. 320).

β-Dichloracetone, $CH_3.CO.CHCl_2$, which is best prepared by passing chlorine into acetone until it is saturated, heating the liquid in the water bath towards the close of the operation, also boils at about 120° (248° F.); it is said that its vapour, like that of monochloracetone, exerts a most irritating action on the eyes and nose, but according to Fittig and Borrche this is due to the presence of impurities. According to Linnemann and V. Zotta, it is converted into ordinary lactic acid when heated with water at 200° (392° F) It combines with hydrocyanic acid, and the resulting cyanide yields *dichloroxyisobutyric acid*, $CH_3.C(CHCl_2)(OH).COOH$, on digestion with hydrochloric acid (Bischoff).

a-Dichloracetone: $CH_2Cl.CO.CH_2Cl$, is obtained by oxidation of dichlorisopropylic alcohol or dichlorhydrin (p. 541) with chromic acid mixture; it boils at about 170° (338° F.). It forms a crystalline compound with sodic hydric sulphite—with which β-dichloracetone also unites—and yields crystalline products with potassic iodide, potassic thiocyanate, and potassic cyanide, the last-named substance converting it into a cyano-derivative of the composition $\left.\begin{matrix}C(CH_2Cl)_2(OH)\\C(CH_2Cl)_2(CN)\end{matrix}\right\}O$, analogous to that formed by acetone, and isomeric with the compound produced in a similar manner from β-dichloracetone (Glutz and Fischer, *ibid.*, iv. 52).

By oxidation of chlorobromhydrin, $CH_2Cl.CH(OH).CH_2Br$, the corresponding *a-chlorobromacetone*, $CH_2Cl.CO.CH_2Br$, is obtained; it is a crystalline substance, which melts at about 35° (95° F.), boils at about 180° (356° F.), and combines with sodic hydric sulphite (Theegarten, *Deut. chem. Ges. Ber.*, vi. 1276).

According to Barbaglia (*ibid.*, vii. 4671), the product of the action of chlorine on well-cooled acetone contains a crystalline body of the composition of dichloracetone, which is deposited in large prisms from the portion boiling at 140°—170° (284°—338° F.); the same substance was obtained by Markownikoff on oxidation of dichlorhydrin. It melts at 44° (111°·2 F.), and probably is a polymeride of dichloracetone (comp. Bischoff, *ibid.*, viii. 1329, and Grabowski, *loc. cit.*).

Pure acetone, saturated with chlorine in the cold, absorbs a further quantity of the gas in sunlight and on warming, especially if the chlorine be moist, forming trichloracetone, but the chlorination does not proceed further (Bischoff, *loc. cit.*). It is a colourless oil, boiling at about 171° (338° F.), which combines with water with great avidity to form a crystalline hydrate, $C_3H_3Cl_3O + {}_2(2CH_2)OH_2$, melting at about 44° (111°·2 F.), from which it may be separated by the action of hydrochloric acid gas (Krämer, *ibid.*, vii. 2561; Bischoff, viii. 1336). It does not combine with acid sulphites; on warming it with aniline and potassic hydrate, phenylic isocyanide is produced, showing that it yields chloroform on decomposition with alkali, and hence that it has the formula $CH_3.CO.CCl_3$; it combines with hydrocyanic acid, and the product yields *trichloracetonic acid*, $CH_3.C(CCl_3)(OH).COOH$, on digestion with hydrochloric acid (Bischoff).

By saturating a solution of acetone in methylic alcohol with chlorine, fractionating the product, and strongly cooling the various fractions of the portion boiling at 160°—180° (320°—356° F.) in contact with water, Bischoff has succeeded in separating the hydrate of tetrachloracetone from that of trichloracetone, and from a mixed hydrate of tri- and tetrachloracetone of the formula $C_3H_2Cl_4O + C_3H_3Cl_3O + 6H_2O$. *Tetrachloracetone*, $CH_2Cl\ CO.CCl_2$, separated from the hydrate by means of hydrochloric acid, is an extremely volatile substance possessing a most irritating odour, the irritation which is frequently experienced on working with the chlorinated derivatives of acetone being probably mainly caused by it. The hydrate, $C_3H_2Cl_4O + 4OH_2$, melts at about 39° (102°·2 F.). A corresponding dibromodichloracetone is formed by the action of bromine on dichlorhydrin (comp. p. 542).

Pentachloracetone, according to Staedeler, is formed by the action of a mixture of potassic chlorate and hydrochloric acid on a number of substances, amongst others citric, salicylic, gallic and quinic acids, quinone, pyrogallol, albumin and muscular flesh. It is a colourless oil, boiling at about 190° (374° F.), which forms a crystalline hydrate with 4 mols. water. *Hexachloracetone* is produced by the action of chlorine in sunshine on a solution of citric acid, which yields acetone on oxidation; it boils at about 200° (392° F.), and forms a crystalline hydrate with 1 mol. of water.

The action of bromine on acetone gives rise in the first instance to the production of a highly unstable additive compound, $C_3H_6OBr_2$ (Linnemann), and subsequently of substitution derivatives. The mono- and dibromo-derivatives are liquids which decompose on distillation; they combine with acid sulphites (Emmerling, *ibid.*, vi. 22; Lokolowsky, ix. 1687). *Pentabromacetone*, obtained by the action of an excess of bromine on acetone (Mulder), is identical with the so-called bromoxaform of Cahours formed by the action of bromine on solutions of citrates, and with the parabromalide of Cloez (Grimaux; comp. pp. 425—461). It crystallizes in lustrous silky needles which melt at 75° (165° F.).

Hexbromacetone.—$CBr_3.CO.CBr_3$ (foot note, p. 797), crystallizes in prisms melting at 108° (226°·4 F.); it is readily decomposed by ammonia in accordance with the equation: $CBr_3.CO.CBr_3 + NH_3 = HCBr_3 + CBr_3.CO.NH_2$.

β-Diiodacetone (?), $CH_3.CO.CHI_2$, is produced by gently heating acetone with an aqueous solution of iodine monochloride; it is a heavy oil, which readily decomposes with separation of iodine (Maxwell Simpson). *a-Diiodacetone*, $CH_2I.CO.CH_2I$, according to Glutz and Fischer, is crystalline.

(1675) HOMOLOGUES OF DIMETHYL KETONE.—A considerable number of ketones homologous with acetone have been prepared, but with few exceptions, only their behaviour on oxidation and with acid sulphites has been ascertained. They have mostly been obtained either by the action of zinc organo-metallic compounds on acid chlorides, or by distillation of the calcic salts of acids of the acetic series. Two only which are especially interesting need therefore be described.

(1676) METHYL TERTIARY-BUTYL KETONE; *pinacolin:* $C_6H_{12}O = C(CH_3)_3.CO.CH_3$.—This ketone was discovered by Fitting in 1859, who obtained it by distilling pinacone or tetramethylglycol (1502) with dilute sulphuric acid (comp. p. 773); its nature was not ascertained, however, until 1873—1874, when Friedel and Silva (*Compt. Rend.*, lxxvii. 48) converted it by oxidation into an acid of the same composition as valeric acid, $C_5H_{10}O_2$, which they termed "*pivalic acid*," but which Butlerow shortly afterwards proved to be *trimethacetic acid*, $C(CH_3)_3.COOH$, the same chemist forming pinacolin itself by the action of zincic methide on trimethacetic chloride (*Ann. Chem. Pharm.*, clxxiii. 355; clxxiv. 125). It is a colourless liquid of peppermint-like odour, almost insoluble in water, boiling at 106° (222°·8 F.); as already mentioned, it yields trimethacetic acid on oxidation, but it is only slowly attacked by the ordinary chromic acid mixture. It does not combine with acid sulphites. It yields a crystalline dichlorinated derivative on treatment with chlorine (Fittig, *ibid.*, cxiv. 54).

(1677) METHYLNONYL KETONE: $C_{11}H_{22}O = CH_3.CO.C_9H_{19}^{a}$.—This ketone, which may be artificially produced by distilling a mixture of the calcium salts of acetic and decylic or capric acids, is the chief constituent of the volatile oil of garden rue (*Ruta graveolens*). It is a colourless strongly refracting oil, boiling constantly at 224° (435°·2 F.); when cooled to 5°—6° (41°—42°·8 F.) it forms a crystalline mass which melts at 15°—16° (59°—60°·8 F.) (Gorup Besanez and Grimm, *ibid.*, clvii. 275). According to Giesecke (*Zeits. Chem.* [2], vi. 428), it is readily oxidized by chromic acid mixture, yielding acetic and nonylic or pelargonic acids, $C_8H_{17}.COOH$; whilst nascent hydrogen converts it into nonylmethylcarbinol, $CH_3.CH(OH).C_9H_{19}$, and a body of very high boiling point which is probably the corresponding pinacone. Nonylmethylcarbinol is a viscid liquid, insoluble in water, boiling at about 228° (442°·4 F.).

(1678) The following table is a list of the ketones of the $(C_nH_{2n+1})_2CO$ series at present known:

C_3H_6O		$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\end{cases}$ Dimethyl ketone. B.P. 56°					
C_4H_8O	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_2H_5}\end{cases}$ Methylethyl ketone. B.P. 81°						
$C_5H_{10}O$	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_3H_7}\end{cases}$ Methylpropyl ketone. B.P. 101°	$\mathrm{CO}\begin{cases}\mathrm{C_2H_5}\\ \mathrm{C_2H_5}\end{cases}$ Diethyl ketone. B.P. 101°	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH(CH_3)_2}\end{cases}$ Methylisopropyl ketone. B.P. 94°				
$C_6H_{12}O$	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_4H_9}\end{cases}$ Methylbutyl ketone. B.P. 127°					$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C(CH_3)_3}\end{cases}$ Methyl tertiary butyl ketone. B.P. 106°	
$C_7H_{14}O$	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_5H_{11}}\end{cases}$ Methylpentyl ketone. B.P. 156°	$\mathrm{CO}\begin{cases}\mathrm{C_3H_7}\\ \mathrm{C_3H_7}\end{cases}$ Dipropyl ketone. B.P. (?) 144°	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_2.CH_2.CH(CH_3)_2}\end{cases}$ Methylisoamyl ketone. B.P. 144°	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH(C_2H_5)_2}\end{cases}$ Methyl secondary amyl ketone. B.P. 138°	$\mathrm{CO}\begin{cases}\mathrm{CH(CH_3)_2}\\ \mathrm{CH(CH_3)_2}\end{cases}$ Diisopropyl ketone. B.P. 125°	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C(C_2H_5)(CH_3)_2}\end{cases}$ Methyl tertiary amyl ketone. B.P. 132°	$\mathrm{CO}\begin{cases}\mathrm{C_2H_5}\\ \mathrm{C(CH_3)_3}\end{cases}$ Ethyl tertiary butyl ketone. B.P. 126°
$C_8H_{16}O$	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_6H_{13}}\end{cases}$ Methylhexyl ketone. B.P. 181°						$\mathrm{CO}\begin{cases}\mathrm{C_2H_5}\\ \mathrm{C(C_2H_5)(CH_3)_2}\end{cases}$ Ethyl tertiary amyl ketone. B.P. 151°
$C_9H_{18}O$					$\mathrm{CO}\begin{cases}\mathrm{CH_2.CH(CH_3)_2}\\ \mathrm{CH_2.CH(CH_3)_2}\end{cases}$ Diisobutyl ketone. B.P. 181°		
$C_{11}H_{22}O$	$\mathrm{CO}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_9H_{19}}\end{cases}$ Methylnonyl ketone. M.P. 15°; B.P. 226°	$\mathrm{CO}\begin{cases}\mathrm{C_5H_{11}}\\ \mathrm{C_5H_{11}}\end{cases}$ Dipentyl ketone. M.P. 14°·6; B.P. 227°					
$C_{13}H_{26}O$		$\mathrm{CO}\begin{cases}\mathrm{C_6H_{13}}\\ \mathrm{C_6H_{13}}\end{cases}$ Dihexyl ketone. M.P. 30°; B.P. 255°					
$C_{19}H_{38}O$		$\mathrm{CO}\begin{cases}\mathrm{C_9H_{19}}\\ \mathrm{C_9H_{19}}\end{cases}$ Dinonyl ketone. M.P. 58°; B.P. above 330°					

§ II. KETONES OF THE $CO\begin{cases}C_nH_{2n+1}\\C_nH_{2n-7}\end{cases}$ AND $CO(C_nH_{2n-7})_2$ SERIES.

(1679) The following ketones of the $C_nH_{2n+1}.CO.C_nH_{2-7}$ series are known:

		B. P. °C.
Methylphenyl ketone . . .	$CH_3.CO.C_6H_5$	200°
Ethylphenyl ketone	$C_2H_5.CO.C_6H_5$	209°
Methylbenzyl ketone . . .	$CH_3.CO.CH_2.C_6H_5$	215°
Propylphenyl ketone . . .	$C_3H_7^{\alpha}.CO.C_6H_5$	221°
Isopropylphenyl ketone . . .	$C_3H_7^{\beta}.CO.C_6H_5$	below 217°
Ethylbenzyl ketone	$C_2H_5.CO.CH_2.C_6H_5$	226°
Methylphenethyl ketone . . .	$CH_3.CO.CH_2.CH_2.C_6H_5$	236°
Isobutylphenyl ketone . . .	$(CH_3)_2.CH.CH_2.CO.C_6H_5$	226°
Isopropylbenzyl ketone . . .	$C_3H_7^{\beta}.CO.CH_2.C_6H_5$	—

With the exception of methylphenethyl ketone, these have all been prepared by distilling mixtures of the calcic salt of benzoic, or of phenylacetic ($C_6H_5.CH_2.COOH$) acid, with the calcic salt of an acid of the acetic series. Methyl and ethylphenyl ketones have also been obtained by the action of zincic methide and ethide respectively on benzoic chloride, $C_6H_5.COCl$, ethylbenzyl ketone having been prepared in a similar manner from phenylacetic chloride, $C_6H_5.CH_2.COCl$. Methylphenethyl ketone is the product of the action of alkalies on ethylic acetobenzylacetate, $CH_3.CO.CH\begin{cases}CH_2.C_6H_5\\COOC_2H_5\end{cases}$. Methyl- and ethylbenzyl ketone and methylphenethyl ketone are the only ones which form compounds with acid sulphites.

METHYLPHENYL KETONE or *acetophenone* crystallizes in large colourless plates which melt at 14° (57°·2 F.), and it boils at about 200° (372° F.). It yields carbonic anhydride, water, and benzoic acid on oxidation (Popoff). By the action of ammonia at the boiling temperature in presence of phosphoric anhydride, it is converted into a crystalline highly stable basic compound, (?) $C_{24}H_{19}N$ (Engler and Heine), a small quantity of triphenylbenzene, which is more readily obtained by the action of hydrochloric acid (p. 778), being also produced. By acting on it with chlorine at the boiling point, it is converted into chloromethylphenyl ketone, $CH_2Cl.CO.C_6H_5$, from which the acetate and corresponding alcohol may be prepared (Graebe; comp. Hunaeus and Zincke, *Deut. chem. Ges. Ber.*, x. 1486). Bromine at ordinary temperatures forms the two isomeric compounds $C_6H_5.CO.CH_2Br$ and $C_6H_4Br.CO.CH_3$ (Emmerling and Engler, *ibid.*, iv. 147).

The remaining members of the series are liquids. *Ethylphenyl ketone* and *methylbenzyl ketone* yield benzoic and acetic acids on oxidation, whilst *ethylbenzyl ketone* forms benzoic and propionic acids (Popoff, *ibid.*, v. 500). *Propylphenyl ketone* yields benzoic and propionic acids (Schmidt and Fieberg, *ibid.*, vi. 498), whilst *isopropylphenyl ketone* yields benzoic and acetic acids, the latter being doubtless formed from the acetone which is the primary product of oxidation. *Methylphenethyl ketone* also yields only benzoic acid and carbonic anhydride, the phenylacetic acid which is first produced being at once further oxidized (Ehrlich, *Ann. Chem. Pharm.*, clxxxvii. 18). *Isopropylbenzyl ketone*, however, yields benzoic and isobutyric acids (Popoff and Fuchs, *ibid.*, ix. 1605), which are also obtained on oxidation of isobutylphenyl ketone.

On reduction, methylphenyl ketone yields both methylphenylcarbinol (1479) and dimethyldiphenylglycol, $(C(CH_3)(C_6H_5)OH)_2$, a crystalline substance which melts at about 120° (248° F.) (Emmerling and Engler, *ibid.*, vi. 1005); ethylphenyl ketone behaves similarly (1480), and propylphenyl ketone also yields the corresponding monohydric alcohol, together with the dihydric alcohol homologous with hydrobenzoin: the latter crystallizes in long needles melting at 64° (147°·2 F.).

(1680) The $CO(C_nH_{2n-7})_2$ series includes the following:

		M. P.	B. P. ° C.
Diphenyl ketone . . .	$C_6H_5.CO\,C_6H_5$	26° and 49°	300°
Paraphenyltolyl ketone .	$C_6H_5.CO.C_6H_4.CH_3$	57°	314°
Orthophenyltolyl ketone .		—	—
Phenylbenzyl ketone . .	$C_6H_5.CO.CH_2.C_6H_5$	55°	—
Paraditolyl ketone . . .	$CH_3.C_6H_4.CO.C_6H_4\,CH_3$	95°	—
Dibenzyl ketone . . .	$C_6H_5.CH_2.CO.CH_2.C_6H_5$	30°	320°
Phenylcymyl ketone . .	$C_6H_5.CO.C_6H_3(CH_3)(C_3H_7)$[a]	—	340°

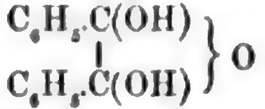
Diphenyl ketone is formed by distillation of calcic benzoate; by heating mercury diphenyl with benzoic chloride at 180° (356° F.): $Hg(C_6H_5)_2 + 2C_6H_5\,COCl = (C_6H_5)_2CO + HgCl_2$ (Otto); by heating a mixture of benzene, benzoic acid and phosphoric anhydride at about 180° (356° F.) (Kollarits and Merz, *ibid.*, v. 447; vi. 536); by the action of carbonic chloride, $COCl_2$, on benzene in presence of aluminic chloride (Friedel, Crafts and Ador, *ibid.*, x. 1854); and by oxidation of diphenylmethane (1377), diphenylcarbinol (p. 503), and diphenethaldehyde. When prepared by oxidation of diphenylmethane, it is first obtained as a clear liquid, which on standing becomes a mass of apparently monoclinic crystals resembling the forms produced by cleavage of Iceland spar, and melting at about 26° (78°·8 F.): after a time, however, the crystals become milk-white, and are converted into the rhombic prisms in which the ketone ordinarily separates from its solutions, and which melt at about 48° (118°·4 F.) (Zincke, *ibid.*, iv. 576). According to Linnemann (*Ann. Chem. Pharm.*, cxxxiii. 1), it is converted into *diphenylcarbinol* or *benzhydrol* by the action of sodium amalgam on its alcoholic solution; whereas if zinc and sulphuric acid are employed, chiefly *tetraphenylglycol* or *benzopinacone*, $(C(C_6H_5)_2.OH)_2$, is obtained. Benzopinacone crystallizes from alcohol in small well-formed prisms; it melts at 186° (366°·8 F.), being, however, decomposed into diphenyl ketone and benzhydrol; the same decomposition is effected by boiling it with an alcoholic solution of potassic hydrate (Thörner and Zincke, *Deut. chem. Ges. Ber.*, x. 1473). On treatment with benzoic chloride, benzopinacone is apparently converted into the ketone $C_6H_5.CO.C(C_6H_5)_3$. A number of substitution derivatives of diphenyl ketone have been obtained.

Di-dimethylamidophenyl ketone.—Although carbonic chloride, $COCl_2$, alone is entirely without action on benzene even at high temperatures, it readily acts on dimethylamidobenzene or dimethylaniline, $C_6H_5.N(CH_3)_2$, forming *dimethylamidobenzoic chloride*, $(CH_3)_2N.C_6H_4.COCl$, the reaction taking place even in the cold. On heating this product with dimethylaniline at about 120° (248° F.), the diphenyl ketone derivative $CO[C_6H_4.N(CH_3)_2]_2$ is produced, together with the compound, $(CH_3)_2N.C_6H_3[CO\,C_6H_4.N(CH_3)_2]_2$, formed by the action of 2 mols. of the chloride on a single mol. of dimethylaniline (Michler, *ibid.*, ix. 7161).

Tolylphenyl ketones.—These are formed on oxidation of the benzyltoluenes (p. 362), and on heating a mixture of benzoic acid and toluene with phosphoric anhydride; the para-compound, which alone has been obtained pure, is also formed on distillation of a mixture of calcic benzoate and paratoluate. They are converted into the corresponding benzoylbenzoic acids on oxidation. On reduction with zinc and hydrochloric acid, paratolylphenyl ketone yields two isomeric crystalline compounds of the formula $C_{28}H_{24}O$, melting respectively at 137° (278°·6 F.) and 215° (419° F.), the dihydric alcohol $C_{28}H_{26}O_2$ or $[C(C_6H_5)(C_6H_4.CH_3).OH]_2$, which is first produced, undergoing conversion into these compounds under the influence of the zincic chloride. Thörner has shown (*Ann. Chem. Pharm.*, clxxxix. 96) that the body of lower is very easily transformed into that of higher melting point by heating with hydrochloric, hydriodic, or acetic acid at about 150° (302° F.), or on warming with benzoic chloride, and that on oxidation it is reconverted into the ketone; whereas the isomeride yields an acid of the composition $C_{22}H_{20}O_2$ (comp. p. 773). The alcohol $C_{28}H_{26}O_2$ closely resembles benzopinacone in its properties (Thörner and Zincke, *loc. cit.*).

Phenylbenzyl ketone: $C_6H_5.CO.CH_2.C_6H_5$, obtained by distillation of a mixture of benzoate and phenylacetate of calcium, is identical with the so-called *deoxybenzoin* formed by reduction of benzoin, and by oxidation of benzylphenylcarbinol or toluylenehydrate (p. 503) (Radziszewski, *ibid.*, viii. 756); it is also produced on heating a mixture of benzene and phenylacetic acid with phosphoric anhydride (Zincke, *ibid.*, ix. 1771). It crystallizes from alcohol in large colourless plates, melting at 55° (131° F.); on oxidation it yields benzoic acid.

Benzoin or *benzoylphenylcarbinol:* $C_6H_5.CO.CH(C_6H_5).OH$, is obtained on oxidation of hydrobenzoin with concentrated nitric acid, and by the action of an alcoholic solution of potassic cyanide on benzaldehyde (p. 758). It crystallizes in colourless prisms, melting at 134° (273°·2 F.), difficultly soluble in water and alcohol; on oxidation with chromic acid mixture it yields benzoic aldehyde and benzoic acid, but nitric acid converts it into *benzil* or *dibenzoyl*, $C_6H_5.CO.CO.C_6H_5$. Benzil crystallizes from alcohol in large six-sided prisms, melting at 90° (194° F.). On oxidation, it is entirely converted into benzoic acid, and on reduction forms benzoin; it dissolves in a concentrated alcoholic solution of potassic hydrate forming a deep violet-coloured liquid, which after prolonged warming becomes yellow. Under these circumstances isomeric change takes place, the benzil being converted into the potassic salt of diphenylglycolic or benzilic acid, $(C_6H_5)_2C(OH).COOH$. The formation of this acid is probably preceded by that of the compound:



$$\left.\begin{array}{l} C_6H_5.C(OH) \\ \qquad\quad | \\ C_6H_5.C(OH) \end{array}\right\} O$$

to which perhaps the violet colour is due, the subsequent change being analogous to that which results in the formation of the so-called pinacolins (p. 773).

Paraditolyl ketone, obtained by oxidation of ditolylmethane (p. 363), crystallizes from alcohol in rhombic prisms, melting at 95° (203° F.); it is converted into ditolylcarbinol, $(CH_3.C_6H_4)_2C_6(OH)$, on reduction (Weiler). The isomeric *dibenzyl ketone* is prepared by distillation of calcic phenylacetate (Radziszewski).

Phenylcymyl ketone is produced on heating a mixture of benzene and cymene with phosphoric anhydride (Kollarits and Merz, *loc. cit.*); it is an oily liquid of pleasant odour.

§ III. KETONES OF OTHER SERIES.—CAMPHOR.

(1681) NAPHTHYL KETONES.—By heating a mixture of benzoic acid and naphthalene, or of benzene and α- or β-naphthoic acid, with phosphoric anhydride, Kollarits and Merz have obtained two phenylnaphthyl ketones, $C_6H_5.CO.C_{10}H_7$. The α-compound is the more soluble in alcohol, from which it crystallizes in short prisms, melting at 75°·5 (167°·9 F.); the β-ketone forms long needles, melting at 82° (179°·6 F.). Michael and Adair (*ibid.*, x. 583) have obtained the same compounds by heating a mixture of benzenene sulphonic acid and naphthalene with phosphoric anhydride, but state that they melt at 100° (212° F.) and 116° (240°·8 F.) respectively.

Similarly, on heating *a*-naphthoic acid with naphthalene and P_2O_5, or *a*-naphthoic chloride and naphthalene with zinc, or *β*-naphthoic chloride with mercury dinaphthyl, $Hg(C_{10}H_7)_2$, *a*-*β*-dinaphthyl ketone, $C_{10}H_7{}^{a}.CO.C_{10}H_7{}^{\beta}$, is produced. This crystallizes in needles, melting at 135° (275° F.), and when decomposed by heating with soda lime yields both *a*- and *β*-naphthoic acids and naphthalene. By heating *β*-naphthoic acid and naphthalene with P_2O_5, or *β*-naphthoic chloride and naphthalene with zinc, two ketones isomeric with the *a*-*β* compound are produced, both of which, however, yield *β*-naphthoic acid and naphthalene when heated with soda lime; they melt at 126°·5 (259°·7 F.) and 165° (329° F.) respectively, and require for complete solution, the one 267, and the other 1250 parts of absolute alcohol at 19° (66°·2 F.), the *a*-*β* ketone dissolving in 77 pts. (Grucarevic and Merz, *ibid.*, vi. 1238, 1246; ix. 1515).

(1682) **MESITYL OXIDE**: $C_6H_{10}O = (CH_3)_2C{=}CH.CO.CH_3$.—This ketone, as already mentioned, is formed by "condensation" of 2 mols. of dimethyl ketone, which takes place under the influence of hydrochloric and sulphuric acids (Kane), of alkalies and of lime (Fittig), of zincic methide and ethide (Pawlow), and of several other substances. The product obtained in the preparation of acetone by the action of zincic methide on acetic chloride consists chiefly of mesityl oxide, and homologous compounds are obtained in a similar manner in the preparation of the homologues of acetone (Pawlow, *Ann. Chem. Pharm.*, clxxxviii. 126). It is best prepared by the action of hydrochloric acid (Baeyer; Claissen, *ibid.*, clxxx. 4).

Mesityl oxide is a colourless liquid, boiling at 130° (266° F.), having an odour of peppermint; it does not combine with acid sulphites. On oxidation with nitric acid, it yields acetic and oxalic acids; on reduction with sodium amalgam, it is converted into an oily body of the composition $C_{12}H_{20}O$, which is perhaps the corresponding pinacolin; and it combines with bromine, forming a highly unstable dibromide (Claissen). It also unites with hydriodic acid (Pawlow), and with hydrochloric acid, but the compounds are extremely unstable; if it is saturated with hydrochloric acid, and the resulting product, after washing with water, be digested with an alcoholic solution of potassic cyanide, and the solution then heated with an alkali, a crystalline acid of the formula $C_8H_{13}NO_3$ is obtained, from which the nitrogen is not eliminated in the form of ammonia on boiling with alkali, neither is it displaced by the action of nitrous acid (Maxwell Simpson, *Ann. Chem. Pharm.*, cxlviii. 351). Mesityl oxide yields mesitylene on treatment with concentrated sulphuric acid, but it is doubtful whether this hydrocarbon is formed merely by the withdrawal of the elements of a molecule of water, as by boiling with very dilute sulphuric acid it is completely reconverted into dimethyl ketone (Claissen).

Three (?) ketones isomeric with mesityl oxide have been described: *metacetone*, *dumasin*, and *allylacetone*. *Metacetone* was first obtained by Fremy on distillation of sugar, charcoal, and gum with lime (comp. Benedikt, *ibid.*, clxii. 303). It boils at about 84° (183°·2 F.), and on oxidation yields acetic and propionic acids; it does not combine with acid sulphites; phosphoric pentachloride and most of the ordinary reagents decompose it more or less completely. As it yields propionic acid on oxidation, it does not appear probable that it is formed by condensation of dimethyl ketone, as has been supposed; a compound formed by condensation of ethaldehyde and methylethyl ketone: $CH_3.COH + CH_3.CO.C_2H_5 = CH_3.CH{=}CH.CO.C_2H_5$, however, would doubtless exhibit the behaviour of metacetone, and it is quite possible that it is so formed.

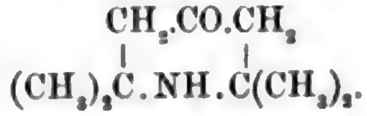
Dumasin is a product of the distillation of acetates; it is a colourless oil, boiling at 120°—125° (248°—257° F.), and forming a crystalline compound with acid sulphites; it yields oxalic acid on oxidation with concentrated nitric acid (comp. Fittig, *ibid.*, cx. 21).

Allylacetone: $CH_3.CO.CH_2.CH_2.CH{=}CH_2$, is obtained on decomposing ethylic allylacetoacetate, $COOC_2H_5.CH\begin{cases}CO.CH_3\\CH_2.CH{=}CH_2,\end{cases}$ with alkalies; it is a colourless liquid, boiling at 128°—130° (262°·4—266° F.), which does not combine with acid sulphites, and on oxidation yields acetic and oxalic acids, the isocrotonic acid, $CH_2{=}CH.CH_2.COOH$, which is probably first produced, being further oxidized (Zeidler, *ibid.*, clxxxvii. 34).

The homologue of mesityl oxide, $C_8H_{14}O$, formed in the preparation of methylethyl ketone, boils at about 168° (334°·4 F.); that of the formula $C_{10}H_{18}O$, obtained in the preparation of methylisopropyl ketone, boils at about 190° (374° F.); and that of the formula $C_{12}H_{22}O$, obtained as bye-product in the preparation of methylisobutyl ketone, boils at about 218° (424°·4) (Pawlow).

(1683) METHYLCINNAMYL KETONE: $CH_3.CO.CH{=}CH.C_6H_5$, obtained by distillation of a mixture of calcic acetate and cinnamate, is a colourless oil, boiling at 241° (465°·8 F.); it forms crystalline compounds with acid sulphites (Engler and Leist, *ibid.*, vi. 254).

(1684) PHORONE.—This name is applied to two isomeric bodies of the formula $C_9H_{14}O$, one solid and the other liquid, formed by condensation of acetone. The former is best prepared by the action of hydrochloric acid (Baeyer; Claissen, *loc. cit.*); the latter is a product of the action of sodium (Staedeler), and of lime (Fittig), and is also obtained by distillation of sugar with lime and in a similar manner from camphoric acid (comp. Kachler, *ibid.*, clxiv. 79). The solid body forms large prisms which melt at 28° (82°·4 F.), and boil at 196° (384°·8 F.). On oxidation with chromic acid mixture, it yields acetic and oxalic acids, and on reduction is converted into a crystalline compound of the formula $C_{18}H_{28}O$; it forms a crystalline tetrabromide, $C_9H_{14}OBr_4$, and is resolved into mesityl oxide and acetone by boiling with dilute sulphuric acid (Claissen). It yields pseudocumene, $C_6H_3(CH_3)_3$, on distillation with phosphoric anhydride (Jacobsen, *Deut. chem. Ges. Ber.*, x. 855). Phorone therefore exhibits considerable resemblance to mesityl oxide, and consequently it may be represented by a similar formula, viz., $(CH_3)_2C{=}CH.CO.CH{=}C(CH_3)_2$; *i.e.*, it may be regarded as formed from a molecule of acetone and a molecule of mesityl oxide in the same way that the latter is formed from 2 mols. of the former. This appears to be the most probable formula which can be assigned to phorone, as it is formed on heating nitrosotriacetonamine with potassic hydrate solution (Heintz), triacetonamine being apparently a compound of the formula:



$$\begin{array}{ccc} & CH_2.CO.CH_2 & \\ & | \qquad\qquad | & \\ (CH_3)_2C & .NH. & C(CH_3)_2. \end{array}$$

Liquid phorone boils at about 210° (410° F.); it yields acetic acid and adipic acid, $C_4H_8(COOH)_2$, on oxidation (Kachler), and on treatment with phosphoric anhydride is converted into pseudocumene. The condensation of acetone would appear therefore to take place in a totally different manner, according as acid or alkaline agents are employed; the manner in which the latter act, however, is at present quite obscure.

(1685) ETHYLENEDIETHYL KETONE: $C_2H_4(CO.C_2H_5)_2$; PHENYLENEDIETHYL KETONE: $C_6H_4(CO.C_2H_5)_2$.—The first of these compounds is obtained by the action of zincic ethide on succinic chloride, $C_2H_4(COCl)_2$; the second, in a similar manner, from phthalic chloride. The ethylene ketone is liquid, and cannot be distilled; the phenylene ketone forms large colourless crystals, possessing a fruity odour, which melt at 52° (125°·6 F.); neither combines with acid sulphites (Wischin, *Ann. Chem. Pharm.*, cxliii. 259).

(1686) DIPHENYLENE KETONE: $CO\begin{Bmatrix}C_6H_4\\C_6H_4\end{Bmatrix}$, is formed by distillation of diphenic acid, $C_6H_4(COOH).C_6H_4(COOH)$, with excess of lime, and on oxidation of diphenylenemethane or fluorene (1383). It crystallizes from alcohol in pale yellow plates, melting at 84° (183°·2 F.), and boiling above 300° (572° F.); when carefully fused with potassic hydrate, it is converted into the potassic salt of phenylbenzoic acid, $C_6H_5.C_6H_4.COOH$ (Fittig and Ostermayer, *ibid.*, clxvi. 374).

(1687) CAMPHOR : $C_{10}H_{16}O$.—The nature of this compound is at present far from determined, but as there is some reason to suppose that it belongs to the class of ketones, it may conveniently be described here. *Common* or *laurel camphor* is produced in the island of Formosa and Japan, being obtained from the *Laurus camphora*, a tree which is found throughout Central China and in the Japanese Islands. This variety is dextrorotatory. The oil of feverfew (*Pyrethrum parthenium*) contains a substance which apparently resembles ordinary camphor in all respects excepting that it manifests an optical activity of equal extent, but of opposite sign; the oils of many labiate plants, such as lavender, marjoram, rosemary and sage, are also said to contain camphors, differing merely from ordinary camphor in their behaviour to polarized light, being in somes cases optically inactive. A substance resembling ordinary camphor is formed on oxidation of some of the terpenes (p. 237). None of these (?) isomerides of ordinary camphor have been sufficiently examined, however.

In order to extract the camphor, the wood is cut into small chips, which are then exposed to the vapour of boiling water in a rude kind of still (*vid. Pharmacographia*, p. 461); the crude camphor which volatilizes is usually exported without further purification. The so-called camphor-oil which drains from the crude camphor, according to Beckett and Wright (*Journ. Chem. Soc.*, xxix. 7), is a complex mixture probably containing a terpene, a body having the composition $C_{10}H_{16}O$, and a liquid oil containing less hydrogen than camphor, together with much camphor. Crude camphor is purified in Europe by sublimation in peculiar glass flasks, and is sent into the market as refined camphor in the form of large bowls or concave cakes, each of which has a round hole in the bottom corresponding to the aperture of the vessel in which the sublimation has been conducted.

Camphor is a colourless crystalline solid of peculiar odour, very slightly soluble in water, readily soluble in alcohol, ether, chloroform, carbonic bisulphide, and many other liquids; it melts at 175° (347° F.), and boils at 205° (401° F.), volatilizing rapidly even at ordinary temperatures. By spontaneous and extremely slow sublimation, it may be obtained in lustrous hexagonal plates or prisms. It is extremely tough, and cannot be pulverized *per se*, but if moistened with any of the liquids which dissolve it, pulverization is effected without difficulty. Its apparent sp. rotatory power in solution varies according to the strength of the solution and the nature of the solvent, the value of $[\alpha]_D$ in the case of alcoholic solutions containing 9·68, 30·16, and 54·7 per cent. respectively of their weight of camphor being, for example, 42°·8, 44°·9, and 47°·8; its absolute sp. rot. power determined by the method described on pp. 574—576 being at 20° (68° F.) $[\alpha]_D = 55°·6$ (Landolt, *Deut. chem. Ges. Ber.*, ix. 914).

Camphor does not unite with acid sulphites, nor is it oxidized by prolonged heating with a concentrated solution of potassic dichromate and sulphuric acid. It absorbs hydrochloric acid, sulphurous anhydride, and nitric peroxide gases in quantities varying according to temperature and pressure, forming colourless liquids which are at once decomposed by water (Bineau, *Ann. Chim. Phys.* [3], xxiv. 328); it also unites with hydriodic acid, forming a crystalline compound $C_{10}H_{17}IO$ (Kekulé and Fleischer, *ibid.*, vi. 934); and on treatment with nitric acid, it yields an oily substance of the composition $(C_{10}H_{16}O)_2.N_2O_5$, which is also decomposed by water (Kachler, *Ann. Chem. Pharm.*, clix. 283). It is not affected by the ordinary reducing agents, but if dissolved in an inert liquid such as toluene and heated to about 90° (194° F.) with sodium, it is converted into sodium camphor, $C_{10}H_{15}NaO$, and the hydrogen thus displaced acts on another portion of the camphor forming borneol, $C_{10}H_{17}(OH)$;* by the action of ethylic iodide on sodium camphor, ethylcamphor, $C_{10}H_{15}(C_2H_5)O$, is produced as a colourless liquid, boiling at 226°—229° (438°·8—444° F.) (Baubigny, *Ann. Chim. Phys.* [4], xix. 230). Phosphoric pentachloride readily acts on camphor, displacing its oxygen by chlorine; the resulting compound, $C_{10}H_{16}Cl_2$, is crystalline, and is resolved by slow distillation into hydrochloric acid and cymene, $C_{10}H_{14}$. Camphor also yields cymene on distillation with zincic chloride, or phosphoric anhydride or pentasulphide (Pott; comp. Fittica, *Ann. Chem. Pharm.*, clxxii. 303); in no case, however, is cymene the only product: both lower and higher homologues of this hydrocarbon, viz., toluene, xylene, mesitylene and laurene (p. 296), being formed when zincic chloride is employed; whilst with phosphoric pentasulphide a considerable quantity of thiocymophenol, $C_{10}H_{13}.SH$ (Flesch; Fittica), and of higher and lower homologues of benzene (Armstrong) is produced; apparently the cymene obtained with the aid of phosphoric anhydride is a purer product, but in this case, according to Lippman and Longuinine (*Zeits. Chem.* [2], v. 413, and Rommier (*Compt. Rend.*, lxviii. 930), small quantities of phenol and cresol are formed. By boiling camphor for some time with about one-fifth of its weight of iodine, a considerable amount of carvacrol or orthomethyl metapropylphenol, $C_{10}H_{13}.OH$ (p. 495), is produced (Fleischer and Kekulé, *Deut. chem. Ges. Ber.*, vi. 934); colophene, $C_{20}H_{32}$, and cymene and other hydrocarbons of the benzene series, are also largely formed (Armstrong). By passing its vapour over heated soda lime, or by boiling it with an alcoholic solution of potassic hydrate, and also by the action of potassium on a solution of camphor in petroleum, *campholic acid*, $C_{10}H_{18}O_2$, is produced (Kachler, *Ann. Chem. Pharm.*, clxii. 259). By prolonged boiling with nitric acid of sp. gr. 1·37, camphor is converted into *camphoric acid*, $C_{10}H_{16}O_4 = C_8H_{14}(COOH)_2$, which on further oxidation by nitric acid yields *camphoronic acid*, $C_9H_{12}O_5 =$ (?) $C_7H_9(OH)(COOH)_2$ (Kachler, *ibid.*, clix. 281); by heating camphoronic acid with bromine and water it is converted into oxycamphoronic acid, $C_9H_{12}O_6$, which apparently is also a trihydric dibasic acid (Kachler). According to Kulhem (*ibid.*, clxiii. 231), if the boiling with nitric acid be continued for a long time, a crystalline body, which he terms *dinitroheptylic* (? hex) *acid* $C_6H_{10}(NO_2)_2O_2$, is obtained. The behaviour of these oxidation products is of considerable importance as throwing light on the constitution of camphor itself. Thus on heating camphoric acid with a considerable quantity of a saturated solution of hydriodic acid at 200° (392° F.) it yields the hydrocarbon *hexhydrometaxylene*, $C_8H_{16} = C_6H_{10}(CH_3)_2$, which by oxidation is converted into *isophthalic acid*, $C_6H_4(COOH)_2$, and forms *trinitrometaxylene*, $C_6H(NO_2)_3(CH_3)_2$, on treatment with a mixture of concentrated nitric and sulphuric acids (Wreden, *ibid.*, clxxxvii. 153). By carefully fusing camphoric acid with potassic hydrate it is converted into *pimelic acid*, $C_5H_{10}(COOH)_2$ (Hlasiwetz and Grabowski; Kachler, *ibid.*, clxix. 168); camphoronic acid, when similarly treated, yielding butyric acid in accordance with the equation: $C_7H_{12}O_5 + 2H + OH_2 = 2C_4H_8O_2 + CO_2$, and this acid is also obtained from oxycamphoronic acid (Kachler, *ibid.*, clix. 295). Both camphoronic and oxycamphoronic acids are bodies of remarkable stability, being little acted upon even by prolonged boiling with nitric acid; the former may be heated with bromine at 150° (302° F.) without forming substitution derivatives.

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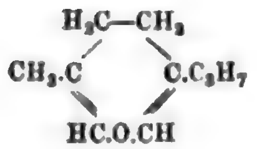
* The compound thus obtained exhibits most of the properties characteristic of the borneol extracted from the *Dryabalanops camphora*, differing only in its optical activity; but different specimens exhibit different rotatory powers (Montgolfier, *Compt. Rend.*, lxxxi. 341; lxxxiv. 445). Borneol much resembles camphor in appearance, but forms brittle crystals melting at 198° (388°·4 F.), and boils at 212° (413°·6 F.); it is converted into camphor by oxidation with nitric acid; hydrochloric acid and phosphoric pentachloride convert it into a crystalline compound, $C_{10}H_{17}Cl$, which melts at 132° (269°·6 F.), and is reconverted into camphor by the action of hypochlorous acid (Kachler). When heated with acids, borneol yields salts such as the stearate $C_{18}H_{35}O_2.C_{10}H_{17}$ (Berthelot).

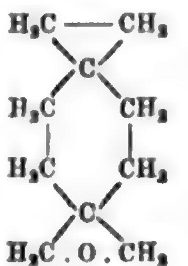
According to Weyl (*Deut. chem. Ges. Ber.*, i. 96), when camphor is heated at 200° (392° F.) with a saturated solution of hydriodic acid, a mixture of three hydrocarbons of the composition C_7H_{16}, $C_{10}H_{18}$ and $C_{10}H_{20}$ is obtained; the hydrocarbon $C_{10}H_{18}$ appears to yield four distinct acids on oxidation, but is chiefly converted into uvitic or methylisophthalic acid, $C_6H_3(CH_3)(COOH)_2$.

Camphor unites directly with bromine to form a crystalline highly unstable dibromide, $C_{10}H_{16}Br_2O$, which splits up on distillation into hydrobromic acid and *monobromocamphor*, $C_{10}H_{15}BrO$; this compound boils at 274°, is easily soluble in alcohol, and crystallizes in prisms, which melt at 76° (168°·8 F.) (525°·2 F.); it is not decomposed by an alcoholic solution of potassic hydrate (Swarts; Perkin). On heating it with bromine at 120° (248° F.), dibromocamphor is produced (Swarts). *Monochlorocamphor*, $C_{10}H_{15}ClO$, is formed by the action of a solution of hypochlorous acid on camphor; according to Wheeler, it melts at 95° (203° F.), and is converted into *oxycamphor*, $C_{10}H_{16}O_2$, by the action of an alcoholic solution of potassic hydrate (*ibid.*, cxlvi. 81). Tetra- and pentachlorocamphor are said to be produced on passing chlorine into a solution of camphor in phosphoric trichloride (Claus).

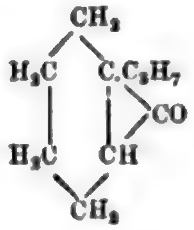
Constitution of camphor.—From the fact that it is not altered by heating with stearic and similar acids (Berthelot), that it does not furnish an acetyl derivative when heated to 230°—250° (446°—482° F.) with acetic chloride or anhydride (Baubigny), and that it exchanges an atom of oxygen for *two* atoms of chlorine when treated with phosphoric pentachloride, there can be little doubt that camphor does not contain the group OH, and therefore that it does not belong to the class of alcohols; moreover, it does not manifest the properties of an aldehyde, as it resists oxidation by chromic acid. The oxygen must therefore be regarded as present either in the form in which it is contained in ethylenic oxide or in the ketones; its conversion into borneol, which has the properties of an alcohol and is readily reconverted into camphor on oxidation, and its general behaviour, are more in accordance with the latter view, which has been adopted by Kachler and Kekulé, and is probably that most generally entertained by chemists. The following formulæ have, however, been proposed at various times for camphor (comp. Kekulé, *Deut. chem. Ges. Ber.*, vi. 929):



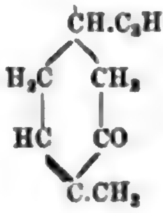
V. Meyer.



Hlasiwetz.

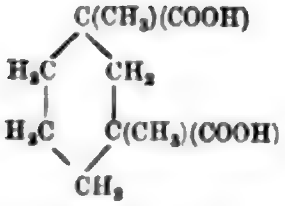


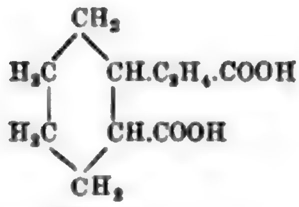
Kachler.

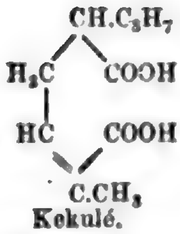


Kekulé.

Hlasiwetz bases his formula on the relation of camphor to the terpenes and on Bauer's synthesis of a terpene from diamylene (1237); he, however, wrongly regards this olefine as a "normal" compound (*ibid.*, iii. 539). Meyer, Kachler, and Kekulé assume the existence of the C_3H_7 group on account of the formation of cymene or paramethylpropylbenzene by the action of dehydrating agents, Kekulé laying especial weight on this transformation of camphor. The formulæ which have been assigned to camphoric acid, which are of importance as showing the manner in which the oxidation of camphor has been supposed to take place, are as follows:


Wreden.


Kachler.


Kekulé.

There are many reasons, however, for doubting the correctness of all these formulæ for camphor and camphoric acid, especially those proposed by Meyer, Kachler and Kekulé. Weyl's observation that the hydrocarbon $C_{10}H_{18}$, obtained by heating camphor with hydriodic acid, yields a methylisophthalic acid ($CH_3 : COOH : COOH = 1 : 3 : 5$), on oxidation cannot be reconciled with the assumption that camphor is a propyl derivative, supposing no isomeric change to take place in the formation of the hydrocarbon; and the fact that the hydrocarbon obtained from camphoric acid by heating it with hydrochloric or hydriodic acid, is a metadimethylbenzene ($CH_3 : CH_3 = 1 : 3$) derivative would appear to necessitate a similar conclusion. Moreover, it is difficult to understand the resistance which camphor opposes to oxidation if it be a propyl derivative, and still less that of camphoronic and oxycamphoronic acids; the fact that bromine is without action on camphoronic acid even at 150° (302° F.) is also worthy of note. But in this respect even if camphor contain the propyl group, the manner in which this group is supposed by Kachler to undergo oxidation appears improbable; and Kekulé's formula for camphoric acid is equally improbable, as it is impossible to explain by it the conversion of the acid into a metaxylene derivative by the action of hydriodic acid, as according to our present experience a reducing agent of this kind would not lead to the formation of a compound in which the chain of carbon atoms is "closed" from one in which it is "open." As Hlasiwetz has pointed out, the formation of cymene from camphor cannot be regarded as absolute proof that the latter is a propyl derivative on account of the simultaneous formation of homologous hydrocarbons, which indeed appear to constitute a very considerable proportion of the entire product in some cases; it may be remembered also that we have pointed out that in the case of the terpenes, the evidence that these compounds are normal propyl derivatives is by no means conclusive, although they readily furnish cymene (p. 290). Kachler does not expressly state that the butyric acid he obtained by fusing camphoronic acid with potassic hydrate was the normal acid, $CH_3.CH_2.CH_2.COOH$; if, however, it is the normal acid which is produced, there is not only evidence that camphor is not a propyl derivative, but it is even probable that radicles of the form (C_nH_{2n+1}) do not enter into its composition; and of all the formulæ which have been proposed, that of Hlasiwetz would appear to approximate most closely to the requirements of theory. Much further study of camphor and its derivatives is necessary, however, and the statements which have been made with regard to the hydrocarbons obtained from it, and the behaviour of its derivatives on fusion with potassic hydrate, must be substantiated before it will be possible to construct a formula which shall exhibit in a satisfactory manner the results of experimental inquiry.

§ IV. QUINONES.

The name quinone was originally applied by Berzelius to the compound $C_6H_4O_2$ first obtained by Woskresensky in 1838 by oxidation of quinic acid, but it is now applied to a number of bodies analogous to it in composition, and which exhibit in a more or less marked degree its peculiar characteristic qualities. The quinones are all derivatives of hydrocarbons of the benzene series or of isologous hydrocarbons, such as naphthalene and anthracene; the view most generally entertained with regard to their constitution, first suggested by Graebe, is that they are formed from these hydrocarbons by the displacement of two atoms of hydrogen by two atoms of oxygen which together act as a dyad radicle. The hydrogen atoms thus displaced are always such as are associated with carbon atoms forming part of a closed chain.

There are three general methods of obtaining quinones.—1. By oxidation of the quinols (hydroquinones)—*i.e.*, the dihydric phenols in which the OH groups occupy relatively the positions 1:4. Thus quinol (hydroquinone), $C_6H_4(OH)_2$, yields quinone, $C_6H_4O_2$. The oxidation is very readily effected, the quinols being at once converted into the corresponding quinones on merely adding nitric acid, or a solution of potassic dichromate and sulphuric acid, to their aqueous solutions, and in many cases mere exposure to the air is sufficient. The reverse change, that of the quinones into quinols, takes place with equal facility, being in most cases effected by means of so feeble a reducing agent as sulphurous acid without the aid of heat, or by digestion with a solution of hydriodic acid and phosphorus. 2. By oxidation of diamido-derivatives of hydrocarbons of the benzene and isologous series, and of amido-derivatives of the monohydric phenols, this being the method most generally available for their preparation. Paradiamidobenzene, $C_6H_4(NH_2)_2$, and paramidophenol, $C_6H_4(NH_2).OH$, for example, both furnish quinone, $C_6H_4O_2$, on oxidation. It is probable that the formation of quinones in this manner is preceded by that of the corresponding alcohols, the amido-group being in the first instance displaced by OH. 3. By oxidation of the corresponding hydrocarbons, as in the formation of anthraquinone, $C_{14}H_8O_2$, from anthracene, $C_{14}H_{10}$, by oxidation with chromic acid. Quinones have not been prepared from hydrocarbons of the benzene series by this method, however; they are doubtless formed in the first instance, but destroyed by further oxidation, as their chlorinated derivatives and chlorinated quinols are obtained when reagents are employed which simultaneously exert an oxidizing and chlorinating action. Thus, when benzene is submitted to the action of a mixture of potassic chlorate and sulphuric acid, both dichloroquinone, $C_6H_2Cl_2O_2$, and trichloroquinol (trichlorhydroquinone), $C_6HCl_3(OH)_2$, are produced.

(1688) **Quinone**; *benzoquinone*: $C_6H_4O_2$.—This compound is formed by oxidation of paradioxybenzene or quinol (hydroquinone), of paradiamidobenzene (paraphenylenediamine), of paramidophenol, and of paramidobenzenesulphonic acid, but not of either of the isomeric dioxy- or diamidobenzenes, amidophenols, or amidobenzenesulphonic acids; also by oxidation of diparamidodiphenyl or benzidine, of amidobenzene or aniline, and of quinic acid, $C_6H_7(OH)_4.COOH$, as well as of coffee and other vegetable substances which furnish quinic acid. It is most readily prepared by oxidizing aniline with sulphuric acid and potassic dichromate (Nietzki, *Deut. chem. Ges. Ber.*, x. 1934).

Quinone crystallizes in long, golden yellow prisms, difficultly soluble in water, but easily in alcohol and ether, melting at 116° (240°·8 F.); it volatilizes at ordinary temperatures and readily in a current of steam; under reduced pressure it may be completely vaporized at the temperature of boiling aniline, when it has a vapour density corresponding to the formula $C_6H_4O_2$ (Hofmann). It possesses a pungent odour, somewhat like that of iodine. A cold aqueous solution of sulphurous acid rapidly transforms it into quinol (hydroquinone), $C_6H_4(OH)_2$, with formation of sulphuric acid. When exposed either alone or in aqueous solution to the air, it gradually becomes brown; and if its aqueous solution be rendered alkaline with ammonia or potassic hydrate, it absorbs oxygen and deposits a brown matter.

HALOID DERIVATIVES OF QUINONE.—Chlorinated derivatives of quinone are obtained by the action of a mixture of potassic chlorate and hydrochloric or sulphuric acid on all substances which furnish quinone on oxidation, and also by direct chlorination of quinone. *Monochloroquinone*, $C_6H_3ClO_2$, is obtained together with the higher chlorinated derivatives of quinone on distilling quinic acid with manganic dioxide, hydrochloric and sulphuric acid; it forms slender yellow needles melting below 100° (212° F.) (Stœdeler). Sulphurous acid converts it into monochloroquinol (monochlorhydroquinone—1512), $C_6H_3Cl(OH)_2$, which is also formed on dissolving it in concentrated hydrochloric acid. *Dichloroquinone*, $C_6H_2Cl_2O_2(O : Cl : O : Cl = 1 : 2 : 4 : 6)$, is most readily prepared by the action of concentrated nitric acid on trichlorophenol (Faust, *Ann. Chem. Pharm.*, cxlix. 149); it is also a product of the action of chlorous anhydride and of chloric acid on benzene (Carius),* and of the oxidation of diorthochloroparamidophenol, $C_6H_2Cl_2(NH_2).OH$. It crystallizes from alcohol in straw-yellow prisms, melting at 120° (248° F.), and readily volatilizes in a current of steam; it yields dichloroquinol on reduction; it dissolves in ammonia, forming a solution which gradually turns green, then reddish, and finally brown, from which acids no longer precipitate the unaltered substance. By the prolonged action of chlorine and of chlor-oxidizing agents on quinone and substances which furnish quinone on oxidation, so-called chloranil is obtained, which was long regarded as tetrachloroquinone; Graebe, however, showed that it was a mixture of tri- and tetrachloroquinone, which cannot be easily separated by the aid of solvents, but may each be obtained in the pure state by digesting the mixture with sulphurous acid and then boiling the product with water, which removes the trichloroquinol, leaving the tetrachloroquinol undissolved; the quinols are then reconverted into the quinones by oxidation, and the latter purified by crystallization (*ibid.*, cxlvi. 1). Graebe prepares chloranil from phenol by the action of potassic chlorate and hydrochloric acid;† according to Stenhouse, (*Jour. Chem. Soc.*, xxi. 141; xxiii. 6), a considerable increase of yield is obtained if the product be submitted to the action of chloride of iodine in presence of water. *Trichloroquinone* forms small yellow prisms, melting at about 165° (329° F.); *tetrachloroquinone* crystallizes in pale-yellow scales, which sublime completely without melting if gently heated, but if suddenly heated it melts, undergoing partial decomposition. Both are insoluble in water, which dissolves mono- and dichloroquinone, and difficultly soluble in alcohol, but more soluble in benzene. Both yield hexachlorobenzene, C_6Cl_6, when heated at 180°—200° (356°—392° F.) with phosphoric pentachloride with addition of phosphoric oxychloride as solvent (Graebe); with acetic chloride, trichloroquinone yields *diacetyltetrachloroquinol*, $C_6Cl_4(O.C_2H_3O)_2$, which is also produced by the action of acetic chloride on tetrachloroquinol at ordinary temperatures (Graebe); when digested with sulphurous acid, or hydriodic acid and ordinary phosphorus (Stenhouse), they furnish the corresponding quinol derivatives; trichloroquinol is scarcely affected by treatment with sodium amalgam and water. Hesse has described a number of remarkable bodies derived from tri- and tetrachloroquinone by the action of sulphites, which have since been examined by Graebe, who has proposed formulæ for them differing somewhat from those assigned to them by their discoverer. Thus on adding tetrachloroquinone to a warm dilute solution of potassic sulphite, two sulpho-salts are produced, one of which Graebe represents as a *dichloroquinoldisulphonate:* $C_6Cl_4O_2 + 3K_2SO_3 + OH_2 = C_6Cl_2(OH)_2(SO_3K)_2 + 2KCl + KHSO_4$; regarding the other as formed by the displacement of the four atoms of chlorine in tetrachloroquinone by the group SO_3K, and the union of the resulting compound with a molecule of hydric potassic sulphite. *Potassic thiochronate*, $C_6(OH)(O.SO_3K)(SO_3K)_4$, as the latter salt is called, is resolved into hydric potassic sulphite and *potassic quinoldisulphonate*, $C_6H_2(OH)_2(SO_3K)_2$, when heated with dilute hydrochloric acid solution at 100° (212° F.); and by the action of alkalies it is converted into the potassic salt of *euthiochronic* or *dioxyquinonedisulphonic acid*, $C_6O_2(OK)_2(SO_3K)_2$. By the action of reducing agents on potassic euthiocronate, the potassic salt of *tetroxybenzenedisulphonic acid*, $C_6(OH)_4(SO_3K)_2$, is produced. Trichloroquinone yields the potassic salt of *trichloroquinolsulphonic acid*, $C_6(OH)_2Cl_2(SO_3H)$, on treatment with potassic sulphite; and by the action of potassic hydrate on this salt in presence of oxygen, the potassic salt of *chlorodioxyquinonesulphonic acid*, $C_6O_2Cl(OK)_2(SO_3K)$, is produced.

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* Krafft has recently shown (*Deut. chem. Ges. Ber.*, x. 797), that the trichlorophenomalic acid of Carius, which was said to be formed in this reaction together with dichloroquinone, is in reality trichloroquinol (trichlorhydroquinone).

† Schreder has observed that the mother-liquors from the preparation of chloranil contain an acid of the formula $CCl_3.C(OH)_2.COOH$, which is also formed from gallic and salicylic acids (*ibid.*, clxxvii. 282).

The chlorine in tri- and tetrachloroquinone is also readily displaced by the action of alkalies; the products of their action have chiefly been studied by Koch, Graebe, and Stenhouse. Thus by dissolving chloranil in a dilute solution of potassic hydrate, it is converted into the potassic derivative of so-called *chloranilic acid* or *dichlorodioxyquinone*, $C_6Cl_2O_2(OH)_2$, which crystallizes in beautiful purple-red prisms; the "acid" itself, which may be obtained by dissolving the salt in water and adding hydrochloric acid, forms bright-red shining scales. By the action of reducing agents, dichlorodioxyquinone is converted into *dichlorodioxyquinol* or *dichlorotetroxybenzene*, $C_6Cl_2(OH)_4$, which crystallizes in colourless needles; it is permanent in the dry state, but when moist absorbs oxygen and is reconverted into the parent compound. Acetic chloride at 100° (212° F.) converts dichlorodioxyquinol into the tetracetyl derivative, $C_6Cl_2(C_2H_3O_2)_4$; and when acted upon by phosphoric pentachloride in the proportion of 1 mol. to 2 mols. of the latter it yields a *tetrachlorodioxybenzene*, $C_6Cl_4(OH)_2$, which differs from tetrachloroquinol in being easily soluble in water and also by yielding a dark-green colour with ferric chloride, the latter circumstance rendering it probable that it is a catechol (pyrocatechin) derivative.

Mono- and dibromo-derivatives of quinone are unknown; a mixture of tribromophenol and tetrabromoquinone is formed by the action of bromine in presence of iodine and water on phenol (Stenhouse). The latter compound closely resembles the corresponding chloroquinone in properties. If bromine is added to water in which bromanilic acid, $C_6Br_2O_2(OH)_2$, is suspended until the latter is dissolved, and the solution is then allowed to stand, crystals are obtained which apparently have the composition $C_6Br_{11}OH$, and a corresponding substance, $C_6Br_8Cl_3OH$, is produced on similar treatment of chloranilic acid (Stenhouse).*

(1689) QUINHYDRONE.—When solutions of quinone and of quinol are mixed together, the two combine forming so-called quinhydrone, which crystallizes from the solution in long flat glistening green-coloured needles; this substance is also formed by incomplete reduction of quinone, and by partial oxidation of quinol. According to Liebermann, it has the composition $C_{12}H_{10}O_4$, as very nearly the theoretical amount is obtained when the quinone and quinol are employed in simple molecular proportions. It dissolves in hot water, and separates almost entirely from the solution on cooling, but is decomposed by boiling with water; reducing agents convert it into quinol, and oxidizing agents into quinone (*Deut. chem. Ges. Ber.*, x. 1614). The bodies homologous and isologous with quinone and their haloid derivatives mostly form similar compounds.

(1690) PHENOQUINONE.—This name has been assigned by Wichelhaus to the compound $C_{18}H_{14}O_4$ formed together with quinol, quinhydrone, and probably other reduction products when quinone is added to a solution of phenol, and also by careful oxidation of phenol (comp. p. 476). When purified by sublimation, it forms beautiful red needles with green metallic lustre, melting at 71° (159°·8 F.); it dissolves in water, and when heated with alkalies or acids is readily resolved into its generators or their products of decomposition. From the manner in which it is formed it probably has the formula $C_6H_4(O.OC_6H_5)_2$.

All the phenols appear to react with quinone in a similar way. Thus on mixing solutions of quinone and pyrogallol, *pyrogalloquinone* at once separates, and the liquid is found to contain only quinol:

$$\underset{\text{Quinone.}}{2C_6H_4O_2} + \underset{\text{Pyrogallol.}}{2C_6H_3(OH)_3} = \underset{\text{Quinol.}}{C_6H_4(OH)_2} + \underset{\text{Pyrogalloquinone.}}{C_6H_4[O.OC_6H_3(OH)_2]_2}$$

This body forms brick-red needles, insoluble in water, melting at about 200° (392° F.).

Probably, also, all the homologues and isologues of quinone which are without difficulty converted into quinols, resemble quinone in their behaviour with phenols. The haloid derivatives of the quinones, however, act somewhat differently, trichloroquinone yielding quinhydrone and pyrogalloquinone, respectively, on treatment with quinol and pyrogallol, whilst tetrachloroquinone is converted into tetrachloroquinol by heating with pyrogallol at 100° (212° F.). Thiophenol also exerts a reducing action on quinone, converting it into quinhydrone and quinol.

By the action of aniline, phenoquinone is converted into the compound

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* The nature of these remarkable products is at present unknown, but it is not improbable that their relation to benzene is less simple than these formulæ indicate, as complex bodies have been obtained by the action of chlorinating and brominating agents on other derivatives of benzene. Thus by the action of bromine in presence of water on triamidophenol, Weidel and Gruber have obtained the compound $C_{18}H_8N_3Br_{11}O_7$, which is converted into the compound $C_{18}H_7Br_{11}O_{11}$ by warming with sulphuric acid, the latter being probably related to the bodies $C_{18}H_2Br_{10}O$, $C_{18}H_4Br_{14}O_6$, &c., obtained in a similar manner by Stenhouse and Groves from catechol and pyrogallol (pp. 525—548); by the continued action of bromine and water, the compound $C_{18}H_8N_3Br_{11}O_7$ is converted into *hexabromacetone*, $CBr_3.CO.CBr_3$, carbonic anhydride and ammonia being the only accessory products (*Deut. chem. Ges. Ber.*, x. 1137). Benedikt also has recently obtained the compound C_6Br_9OH by the action of bromine in presence of water on tribromophloroglucol; this body yields *pentabromacetone* on warming with alcohol (*Ann. Chem. Pharm.*, clxxxix. 165).

$C_{18}H_{16}O_2N_2$, identical with the substance obtained by Hofmann by the action of aniline on quinone, and which may be represented by the formula $C_6H_4(O.NH.C_6H_5)_2$ (Wichelhaus). The action of aniline on tetrachloroquinone, however, is analogous to that of alkalies, the compound $C_6Cl_2O_2(NH.C_6H_5)_2$ being formed (Hofmann).

(1691) Resorquinone.—Catechol and resorcinol, the isomerides of quinol, do not yield substances related to them as quinone is to quinol on oxidation; but as already mentioned (pp. 523, 531), the so-called pentabromoresorcinol obtained by the action of bromine in excess on resorcinol, on warming is converted into the compound $C_6HBr_3O_2$, with loss of two atoms of bromine; this compound, which is isomeric with tribromoquinone, is, perhaps, derived from a body bearing a similar relation to resorcinol that quinone does to quinol. It dissolves easily in alcohol, with difficulty in ether, benzene, &c., crystallizing in small needles, which decompose at about 190° (374° F.); the attempts to combine it with hydrogen and with bromine have been unsuccessful. A similar compound is obtained by the decomposition of the so-called pentabromorcin (Liebermann and Dittler).

(1692) Toluquinone or Methylquinone: $CH_3.C_6H_3O_2$.—This quinone is formed on oxidation of orthometadiamidotoluene: $CH_3.C_6H_3(NH_2)_2$ ($CH_3 : NH_2 : NH_2 = 1 : 2 : 5$) and of orthotoluidine; it closely resembles benzoquinone, crystallizing in golden-yellow scales, which melt at 67° (152°·6 F.); on reduction with sulphurous acid, it is converted into methylquinol, $CH_3.C_6H_3(OH)_2$, which forms colourless needles, melting at 124° (255°·2 F.) (Nietzki, *Deut. chem. Ges. Ber.*, x. 833; 1934).

According to Southworth (*Ann. Chem. Pharm.*, clxviii. 268), metacresol yields only dichlorotoluquinone, and orthocresol a mixture of di- and trichlorotoluquinone, on treatment with potassic chlorate and hydrochloric acid, whilst paracresol does not furnish a quinone derivative; beech-tar creasote, according to Gorup-Besanez, when thus treated, yields a certain quantity of *tetrachlorotoluquinone* (comp. Bräuninger, *ibid.*, clxxxv. 350).

(1693) Xyloquinone.—By oxidizing the portion of crude phenol boiling at 195°—220° (374°—428° F.), Rommier and Bouilhon (*Jahresb.*, 1862, 322) have obtained a substance—the so-called *phlorone*—of the composition of xyloquinone, $C_8H_8O_2$, which crystallized from water in long, very slender yellow needles, melting at about 61° (141°·8 F.). According to Gorup-Besanez, a tetrachlorinated xyloquinone is formed in small quantity on treating certain beech-tar creasotes with hydrochloric acid and potassic chlorate.

(1694) Oxymetaxyloquinone or Oxydimethylquinone: $C_8H_8O_3 = (CH_3)_2C_6H(OH)O_2$.—This compound is formed by the oxidation of diamidomesitylene $(CH_3)_3C_6H(NH_2)_2$. It crystallizes from water in orange-red needles, and like benzoquinone is very volatile, and has a pungent odour; it melts at 103° (217°·4 F.). Its aqueous solution is immediately coloured a magnificent reddish violet by the addition of a trace of any alkaline substance in consequence of the formation of the corresponding metallic derivative, of which several have been prepared; the potassium compound, $C_8H_7(OK)O_2$, forms small black needles extremely soluble in water. On reduction, it yields *trioxymetaxylene*, $(CH_3)_2C_6H(OH)_3$, which crystallizes, with a molecule of water, in large, colourless, flat, apparently monoclinic prisms, melting at 89° (192°·2 F.), whilst the anhydrous compound melts at about 122° (251°·6 F.). It oxidizes on exposure to the air with formation of the corresponding quinhydrone, which crystallizes in needles resembling potassic permanganate, melting at about 143° (289°·4 F.); ferric chloride reconverts it into the oxyquinone. On distillation over heated zinc dust, trioxymetaxylene is reduced to metaxylene (Fittig and Siepermann, *Ann. Chem. Pharm.*, clxxx. 23).

(1695) Cymoquinone or Methylpropylquinone; *thymoquinone:* $C_{10}H_{12}O_2 = C_3H_7{}^{a}.C_6H_2(CH_3)O_2$.—This quinone is formed by oxidation of both thymol- and carvacrolsulphonic acids (p. 494). but is best prepared by distilling the amidothymol obtained by reduction of nitrosothymol with a concentrated solution of ferric chloride. It crystallizes in yellow glistening plates, melting at 45°·5 (113°·9 F.), and boils at about 200° (392° F.) without decomposing (Carstanjen); when kept, however, especially if moist, it appears to be polymerized, being converted into a white porcelain-like substance, which crystallizes from alcohol in long yellowish-white needles, melting at about 200° (392° F.) (Liebermann.) The quinone is extremely volatile, and, like the homologous compounds, possesses a pungent odour. By the action of sulphurous acid, it is first converted into thymoquinhydrone, which crystallizes in black needles, and then into thymoquinol (hydrothymoquinone—1521). It dissolves in a concentrated solution of potassic sulphite heated to about 60° (140° F.), with considerable development of heat, and on cooling the liquid solidifies to a mass of crystals of the sulpho-salt $C_{10}H_{13}O_2(SO_3K)$. This salt yields thymoquinol when boiled with hydrochloric acid; but if the solution is mixed with an alkali and exposed to the air, it absorbs oxygen energetically, and acquires a dark purple-violet colour: on adding an acid, an orange-coloured precipitate of *oxythymoquinone*, $C_{10}H_{11}(OH)O_2$, is obtained; hence it is probable that the salt in question is a *dioxycymenesulphonate*, $C_3H_7^a.C_6H(CH_3)(OH)_2.SO_3K$ (Carstanjen). The homologues of thymoquinone appear to behave in a similar manner with sulphites. Cymoquinone dissolves in concentrated hydrochloric acid, forming monochlorocymoquinol, $C_3H_7^a.C_6H(CH_3)Cl(OH)_2$. On treatment with bromine, it yields mono- and dibromocymoquinone; the former crystallizing in yellow needles, the latter in glistening pale-yellow scales, which melt at 73°·5 (164°·3 F.); dibromocymoquinone does not appear to be acted on by sulphurous acid, although on treatment with tin and hydrochloric acid it is reduced to cymoquinol.

(1696) OXYCYMOQUINONES.—Diamidothymol and diamidocarvacrol hydrochlorides both furnish *oxycymoquinone*, $C_3H_7^a\ C_6H(CH_3)(OH)O_2$, on distillation with a solution of ferric chloride; when purified by sublimation, this substance forms brilliant scarlet-coloured crystals, mixed, however, with orange-coloured needles, which possess the same composition but melt at a lower temperature (Carstanjen). According to Ladenburg and Engelbrecht, however, the lighter-coloured crystals are probably dioxycymoquinone, monoxycymoquinone melting constantly at 169°—172° (336°·2—341°·6 F.). Oxycymoquinone dissolves in alkaline solutions, forming a deep purple-red coloured liquid; on boiling it with potassic hydrate, *dioxycymoquinone*, $C_3H_7^a.C_6(CH_3)(OH)_2O_2$. is formed. This crystallizes in pale-red prisms, melting at 220° (428° F.) (Carstanjen, ***Journ. pr. Chem.*** [2], iii. 63; xv. 398; Liebermann, ***Deut. chem. Ges. Ber.***, ix. 1778; x. 77, 611; Ladenburg and Engelbrecht, ***ibid.***, x. 49, 1218).

(1697) NAPHTHAQUINONE: $C_{10}H_6O_2$.—Naphthalene may be directly converted into this quinone by oxidation with a solution of chromic anhydride in glacial acetic acid (Groves, ***Journ. Chem. Soc.***, xxvi. 209); and it is formed in almost theoretical quantity by oxidation of the diamidonaphthalene prepared by reducing the nitroamidonaphthalene, which melts at 191° (375°·8 F.) (comp. p. 349). It closely resembles the quinones derived from the hydrocarbons of the benzene series, being a bright yellow crystalline substance, possessing a pungent odour, and readily volatile with vapour of water; it melts at about 125° (257° F.) It yields naphthaquinol on reduction (1522): and combines with this compound forming naphthaquinhydrone, $C_{20}H_{14}O_4$, which is a dark purple crystalline substance.

An *oxynaphthaquinone*, $C_{10}H_5(OH)O_2$, has been prepared by boiling the so-called diimidonaphthol (p. 500) with hydrochloric acid. ***Dioxynaphthaquinone*** or ***naphthazarin***, $C_{10}H_4(OH)_2O_2$, is obtained by the action of concentrated sulphuric acid and zinc or of sulphuric acid alone on *a*-dinitronaphthalene

(p. 353) (Liebermann, *Deut. chem. Ges. Ber.*, iii. 905; De Aguiar and Baeyer, *ibid.*, iv. 251, 438); it forms red-brown crystals, having a bright green metallic lustre, and yields a series of coloured metallic derivatives. By acting on dinitro-α-naphthol with potassic chlorate and hydrochloric acid, *dichloronaphthaquinone*, $C_{10}H_4Cl_2O_2$, is produced, which Graebe has shown (*Ann. Chem. Pharm.*, cxlix. 1) exhibits the closest resemblance to tri- and tetrachloroquinone in its reactions.

(1698) β-NAPHTHAQUINONE: $C_{10}H_6O_2$.—By oxidation of amido-β-naphthol Stenhouse and Groves have obtained a substance isomeric with naphthaquinone, crystallizing in slender needles of a bright orange colour, melting at 96° (204°·8 F.); it is much less volatile than the isomeride, but like it is converted into the corresponding quinol on hydrogenation, and yields phthalic acid on oxidation by nitric acid; when it is mixed with a solution of the quinol, dark-coloured crystals are deposited, probably consisting of the quinhydrone (*Jour. Chem. Soc.*, 1877, ii. 52).

(1699) COERULIGNONE OR CEDRIRET: $C_{16}H_{16}O_6$.—In order to purify the crude acetic acid obtained by distillation of wood (beech and birch), it is the practice in some manufactories to add a small quantity of potassic dichromate to the acid separated from the crude calcic acetate by distillation with a stronger acid, and to allow the mixture to stand for some time; the surface of the liquid then becomes covered with a bluish skin, which gradually sinks, forming a blue deposit on the bottom of the vessel containing the liquid. This substance is insoluble in all ordinary solvents, but may be purified by dissolving it in phenol warmed to about 30° (86° F.), and precipitating with alcohol or ether, the precipitate being then repeatedly extracted with boiling alcohol. Coerulignone is thus obtained crystallized in steel-blue glistening needles; it dissolves in concentrated sulphuric acid, forming a magnificent corn-flower-blue coloured solution, the coloration being so intense that the merest trace may be thus recognized. By the action of reducing agents it is readily converted into hydrocoerulignone, $C_{16}H_{18}O_6$, which is reconverted into the parent compound by oxidizing agents. Hydrocoerulignone forms colourless rhombic crystals, soluble in alcohol and benzene, melting at about 190° (374° F.); it yields metallic derivatives, such as $C_{16}H_{16}Na_2O_6$, and corresponding acetyl and benzoyl derivatives. When heated with a concentrated solution of hydrochloric acid to 180°—200° (356°—392° F.), it yields methylic chloride and hexoxydiphenyl (1551). Hydrocoerulignone therefore probably has the formula $C_6H_2(OH)(OCH_3)_2.C_6H_2(OH)(OCH_3)_2$, coerulignoue being the corresponding quinone (Liebermann, *Ann. Chem. Pharm.*, clxix. 221).

The parent substance from which coerulignone is derived is not known in the pure state, but according to Hofmann (*Deut. chem. Ges. Ber.*, viii. 66) it is a phenol-like body contained in the portion of beech-tar boiling at about 270° (518° F.); this portion of beech-tar also contains an oily body of the composition $C_{11}H_{16}O_3$, which may be isolated in a pure state by fractional distillation and crystallization of its sodium derivative. It boils at 285° (545° F.), and on oxidation yields a quinone of the composition $C_8H_8O_4$, crystallizing in long yellow needles, which is converted into the quinol $C_8H_{10}O_4$ by reducing agents, and yields a dibromo-derivative $C_8H_6Br_2O_4$, which forms magnificent red crystals melting at 175° (347° F.) on treatment with bromine.

(1700) TETROXYDIPHENOQUINONE: $C_{12}H_4O_2(OH)_4$, is formed on treatment of hexoxydiphenyl with iodine; it crystallizes in microscopic blue needles resembling coerulignone, soluble in alkalies with a magnificent blue colour (Liebermann, *ibid.*, ix. 1887).

(1701) ETHENEDICYMOQUINONE: $C_{22}H_{26}O_2$, is formed on oxidation of an alkaline solution of ethenedioxycymyl, $CH_2{=}C[C_6H_2(C_3H_7)(CH_3)(OH)]_2$, by potassic ferrocyanide; it forms dark red crystals, and is reconverted into the parent compound by reduction with sulphurous acid (Jäger, *Jour. Chem. Soc.*, 1877, i. 262).

(1702) **Anthraquinone**: $C_{14}H_8O_2 = C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}C_6H_4$.—Anthracene like naphthalene is converted into the corresponding quinone on oxidation, which is best effected on the small scale by means of chromic anhydride, the hydrocarbon being dissolved in glacial acetic acid, and a solution of the anhydride in acetic acid added as long as reduction takes place; the product is then precipitated by water, and purified by distillation or sublimation. Anthraquinone is produced in small quantity together with diphenyl ketone by distillation of calcic benzoate (Kekulé and Franchimont, *Deut. chem. Ges. Ber.*, v. 908), and is also formed by heating a mixture of phthalic chloride and benzene with zinc, by oxidation of orthotolylphenyl ketone (p. 375), and by heating orthobenzoylbenzoic acid, $C_6H_5.CO.C_6H_4.COOH$, with phosphoric anhydride or sulphuric acid (Behr and Dorp, *ibid.*, vii. 578, 805). Dibrom- and dichloranthracene and anthracenedihydride also furnish anthraquinone on oxidation.

Anthraquinone may be crystallized from hot benzene or nitric acid; it melts at 527° (527° F.), and sublimes in yellow needles or prisms; its boiling point is above that of mercury, but below that of sulphur, its vapour density determined by Deville and Troost's method in sulphur vapour corresponding to the formula $C_{14}H_8O_2$ (Graebe). It is an extremely stable substance, being scarcely affected by oxidizing agents; and it is not converted into the corresponding quinol on treatment with sulphurous acid or a dilute solution of hydriodic acid, although this compound (1527) may be obtained on digesting it with a dilute solution of sodic hydrate and zinc dust, in which the quinone gradually dissolves, forming a red-coloured liquid. Anthraquinone is readily reduced, however, by boiling with a concentrated solution of hydriodic acid and phosphorus, and is finally converted into anthracenedihydride, $C_{14}H_{12}$; the formation of this body is preceded by that of *anthranol*, $C_{14}H_9(OH)$, isomeric with the anthrols or anthraphenols discovered by Linke (1489). Anthranol crystallizes from alcohol in yellow needles, melting at 163°—170° (325°·4—338° F.), soluble in alkalies; it is reconverted into anthraquinone by oxidation (Liebermann and Topf, *Deut. chem. Ges. Ber.*, ix. 1201). When fused with potassic hydrate, anthraquinone yields potassic benzoate: $C_{14}H_8O_2 + 2HOK = 2C_6H_5.COOK$; and when distilled over soda-lime it furnishes benzene. By heating with phosphoric pentachloride and some phosphoric oxychloride at 190°—200° (374°—392° F.), the oxygen in anthraquinone is displaced by two atoms of chlorine, but the dichloranthracene thus produced is further chlorinated (Graebe and Liebermann, *Ann. Chem. Pharm., Sup.*, vii. 284; clx. 125). It yields sulpho-acids when heated with sulphuric acid at temperatures above 200° (392° F.). Anthraquinonedisulphonic acid is also formed by the action of oxidizing agents on dichlor- and dibromanthracenedisulphonic acids (Perkin, *Journ. Chem. Soc.*, xxiv. 20).

Haloid and Nitro-derivatives of anthraquinone.—Mono- and dibromanthraquinone are obtained by oxidation of tri- and tetrabromanthracene, dichloranthraquinone being formed in a similar manner from tetrachloranthracene. Bromine is without action on anthraquinone at ordinary temperatures, but at 100° (212° F.) slowly converts it into dibromanthraquinone. These compounds, like anthraquinone, are extremely stable bodies, and do not enter into reaction with the alkaline sulphites, &c., in the manner so characteristic of the haloid derivatives of benzoquinone (Graebe and Liebermann, *loc. cit.*).

Nitric acid alone does not convert anthraquinone into nitro-derivatives, but on heating anthracene with dilute nitric acid a *dinitroanthraquinone*, $C_{14}H_6(NO_2)_2O_2$, is obtained together with anthraquinone. According to Fritzsche, it crystallizes in microscopic quadratic plates, and possesses the property of combining with all the solid hydrocarbons in coal-tar, and hence it is termed Fritzsche's reagent; the compound with anthracene, $C_{14}H_{10}.C_{14}H_6(NO_2)_2O_2$, forms violet coloured laminæ (*Jahresb.*, 1868, 395).

Anthraquinone readily yields a dinitro-derivative, however, on nitration with a mixture of concentrated nitric and sulphuric acids, but the product is apparently isomeric with the before-mentioned body, as it does not yield the violet compound with anthracene. It is said to yield alizarin on fusion with potassic hydrate; coloured substances are obtained from it by the action of concentrated sulphuric acid, and by the action of nitrous acid on the corresponding diamidoanthraquinone (Böttger and Petersen; Liebermann, *Deut. chem. Ges. Ber.*, iv. 226, 230, 301).

(1703) MONOXY-DERIVATIVES OF ANTHRAQUINONE.—Two monoxyanthraquinones and several isomeric di- and trioxyanthraquinones have been prepared, one of the dioxy- and one of the trioxy-derivatives being identical respectively with alizarin and purpurin, the colouring matters derived from madder root (*Rubia tinctorium*).

o–2 *Monoxyanthraquinone:* $C_{14}H_7(OH)O_2$, is obtained as a bye-product of the manufacture of alizarin from anthraquinone, and is also formed on reduction of alizarin, by the action of nitrous acid on alizarinamid, $C_{14}H_6O_2(NH_2)(OH)$, and by heating a mixture of phthalic anhydride and phenol with sulphuric acid. It crystallizes from alcohol in yellow plates or needles, which do not melt at 285° (545° F.), but sublimes at a higher temperature in yellow plates. It yields a considerable quantity of phthalic acid on oxidation with nitric acid. It decomposes baric and calcic carbonates, and yields a red crystalline barium derivative very soluble in water, but does not dye mordanted cotton; its monacetyl derivative crystallizes from alcohol in small yellowish interlaced needles (comp. Liebermann, *Ann. Chem. Pharm.*, clxxxiii. 151).

o–1 or *Erythroxyanthraquinone:* $C_{14}H_7(OH)O_2$.—This isomeride of oxyanthraquinone is formed together with it on strongly heating a mixture of phthalic anhydride and phenol with sulphuric acid. It crystallizes from alcohol in orange-yellow needles, melting at 173°—180° (343°·4—356° F.), but begins to sublime at 150° (302° F.) in long red-yellow needles. With baric hydrate it forms a red precipitate, almost insoluble in water, but it does not yield a coloured lake with alumina. Its solution in sulphuric acid is reddish-yellow, and exhibits a distinct narrow absorption band in the green, which is absent from the spectrum of the solution of the isomeride (Baeyer and Caro, *Deut. chem. Ges. Ber.*, vii. 968).

(1704) o–1 : 2 DIOXYANTHRAQUINONE OR ALIZARIN: $C_{14}H_6(OH)_2O_2$.—According to Schunck's researches, this substance is not present as such in madder roots, but as an amorphous glucoside* (*rubian*); the roots, however, contain a peculiar ferment (*erythrozym*) capable of decomposing this glucoside with formation of alizarin, although no action takes place as long as the plant is living. Acids and alkalies also separate alizarin from rubian; but in all cases, along with the alizarin, other bodies are obtained, of which even the composition has not yet been satisfactorily ascertained; this indeed is true of many of the madder educts. Although the true formula of alizarin and the possibility of its being an anthracene derivative was first recognised by Strecker (*Zeits. Chem.* [2], iv. 263), its relation to this hydrocarbon was first established by Graebe and Liebermann's researches (*Ann. Chem. Pharm., Sup.*, vii. 291). By distilling it with zinc dust these chemists succeeded in obtaining anthracene, and from its resemblance to chloranilic acid they were then led to regard it as a dihydroxyl derivative of anthraquinone—a view which was completely confirmed by the success of their attempt to prepare it by heating dibromanthraquinone with potassic hydrate. This process was soon utilized for the manufacture of alizarin on the large scale, but not long afterwards the more economical and manageable method now employed was introduced, which consists in fusing with an alkali a salt of the sulpho-acid produced by treatment of anthraquinone with Nordhausen sulphuric acid.*

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* A crystalline glucoside termed *ruberythric acid*, which is resolved into alizarin and a glucose on hydration and which perhaps is the form in which alizarin is present in madder root, was first isolated by Rochleder in 1851 (*Ann. Chem. Pharm.*, lxxx. 321); and the same substance apparently was afterwards described under the name of *rubianic* acid by Schunck, who, however, regarded it as an oxidation product of rubian—a conclusion which is by no means established. According to Rochleder's latest statement (*Deut. chem. Ges. Ber.*, iii. 295), ruberythric acid has the formula $C_{20}H_{22}O_{11}$, its decomposition into alizarin and a glucose being represented by the equation: $C_{20}H_{22}O_{11} = C_{14}H_8O_4 + C_6H_{12}O_6 + OH_2$, which, however, appears somewhat doubtful; Graebe

According to Wartha, a small quantity of alizarin is formed on carefully fusing anthraquinone with potassic hydrate; it is also produced on heating a mixture of catechol (pyrocatechin) and phthalic anhydride with concentrated sulphuric acid, and from both the isomeric monoxyanthraquinones by fusion with potassic hydrate (Baeyer and Caro, *Deut. chem. Ges. Ber.*, vii. 968).

Anthraquinone yields a mixture of mono- and disulpho-acids on treatment with sulphuric acid, at least two modifications of the latter being formed (Caro, *ibid.*, ix. 681); hence "crude alizarin" is a mixture of several substances. It was at first supposed that alizarin was formed from a corresponding disulpho-acid, but it is now known that it is derived from a monosulpho-acid, the first product of the action of potassic hydrate on this acid being monoxyanthraquinone, which is subsequently converted into alizarin, merely by the action of the potassic hydrate (comp. Perkin, *Jour. Chem. Soc.*, 1876, i. 851). Each of the disulpho-acids yields in a similar manner a corresponding dioxy-derivative, isomeric with alizarin, each of which may in turn be converted into a trioxy-derivative by further fusion with alkali (Caro; Schunck and Roemer, *loc. cit.*).

Alizarin is almost insoluble in water, but dissolves in alcohol, ether, benzene, carbonic bisulphide, concentrated sulphuric acid, &c.; it separates from its solution in more or less deeply-coloured yellow flocculi, but sublimed alizarin forms beautiful orange-red needles, melting at about 275° (527° F.). It furnishes a series of metallic derivatives, two atoms of hydrogen becoming displaced by the equivalent amount of metal; the alkali-metal derivatives are soluble, but those of other metals insoluble in water. Its solution in alkalies is of a beautiful violet colour; with alumina it forms a red precipitate or lake; with iron salts a purple precipitate. On reduction with potassic hydrate and zinc, it yields tetroxyanthracene, $C_{14}H_6(OH)_4$, which is very readily reconverted into alizarin by mere exposure of the alkaline solution to the air; when oxidized by nitric acid, it

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and Liebermann have suggested that it has the formula $C_{26}H_{28}O_{14}$, and that its decomposition by hydration is represented by the equation: $C_{26}H_{28}O_{14} + 2OH_2 = C_{14}H_8O_4 + 2C_6H_{12}O_6$; but this formula is scarcely reconcileable with the acid characters of the compound, and the fact that it yields coloured precipitates with many metallic salts.

* The history of the discovery of the constitution of alizarin, and of its artificial production, has been well described by Russell (*British Association Reports*, 1873). An interesting account of the mode of dyeing madder colours will be found in Calvert's work on Dyeing and Calico Printing, edited by Stenhouse and Groves (1876. Manchester: Palmer and Howe).

yields a considerable quantity of phthalic acid. By the action of acetic anhydride it is converted into diacetylalizarin, $C_{14}H_6(C_2H_3O_2)_2O_2$, which forms yellow flat needles or plates, melting at 160° (320° F.); on nitration this substance yields a *nitroalizarin*, $C_{14}H_5(NO_2)(OH)_2O_2$, dyeing alumina mordants a bright orange colour, and converted by reduction into *amidoalizarin*, which crystallizes in small black needles dissolving in alcohol to form a beautiful crimson solution (Perkin, *Jour. Chem. Soc.*, 1876, ii. 578). By heating it with bromine at 180°—190° (356°—374° F.), alizarin is converted into *bromalizarin*, $C_{14}H_5Br(OH)_2O_2$, which yields phthalic acid on oxidation (Perkin, *ibid.*, xxvii. 401).

(1705) ISOMERIDES OF ALIZARIN. 0—1 : 4*Dioxyanthraquinone* or *quinizarin*: $C_{14}H_6(OH)_2O_2$.—This isomeride of alizarin is formed on heating a mixture of phthalic anhydride and quinol (hydroquinone) or parachlorophenol with sulphuric acid (Grimm, *Deut. chem. Ges. Ber.*, vi. 508; Baeyer and Caro, *ibid.*, vii. 968; viii. 152; Liebermann and Giesel, *ibid.*, x. 606); and by the action of heat on purpurin (Schunck and Roemer, *Jour. Chem. Soc.*, 1877, i. 674). It closely resembles alizarin, crystallizing in bright red needles which melt at about 194° (381°·2 F.), and yields similar colours with mordants; but its solution in ether or sulphuric acid exhibits a greenish-yellow fluorescence and a well-defined absorption spectrum, which is not the case with alizarin. Both alizarin and quinizarin are converted into purpurin by oxidation with manganic dioxide and sulphuric acid (De Lalande; Baeyer and Caro). Its diacetyl derivative melts at 200° (392° F.).

0—1 : 3*Dioxyanthraquinone* or *purpuroxanthin*: $C_{14}H_6(OH)_2O_2$, is present in small quantity in madder, and may be obtained by heating purpuroxanthic acid, $C_{14}H_5(OH)_2O_2.COOH$, and from purpurin (trioxyanthraquinone) by boiling it with an alkaline solution of stannous hydrate, or by converting it into amidodioxyanthraquinone by means of ammonia and displacing the NH_2 group in the latter compound by hydrogen by the action of nitrous acid (comp. Liebermann, *Ann. Chem. Pharm.*, clxxxiii. 211; Schunck and Roemer, *loc. cit.*). It sublimes very readily in yellowish-red needles, melting at 263° (505°·4 F.), easily soluble in alcohol; it dissolves in baryta-water, forming a yellowish-red solution, and does not yield colours with mordants. By boiling with potassic hydrate solution, it is reconverted into purpurin; on oxidation with nitric acid it yields a considerable quantity of phthalic acid. Its diacetyl derivative forms pale yellow needles, melting at about 184° (363°·2 F.). It yields crystalline dibromo- and dinitro-derivatives (Plath, *Deut. chem. Ges. Ber.*, ix. 1204).

(?) 2′—3 or 2′—2 *Dioxyanthraquinone; Anthraflavic acid*: $C_{14}H_6(OH)_2O_2$.—This isomeride of alizarin is a constituent of the crude, artificially prepared alizarin (Schunck; Perkin, *Jour. Chem. Soc.*, xxiv. 1109; xxvi. 19; Schunck and Roemer, *Deut. chem. Ges. Ber.*, ix. 379, 678); from which it may be extracted by boiling with baryta-water, being the product of the action of alkali on one of the disulpho-acids formed on heating anthraquinone with sulphuric acid (Caro); it is also the chief constituent of the so-called anthraflavone obtained by Barth and Senhofer (*Ann. Chem. Pharm.*, clxx. 100) by heating metaoxybenzoic acid with somewhat dilute sulphuric acid at 180°—200° (356°—392° F.) (Schunck and Roemer, *ibid.*, x. 1225). It crystallizes from alcohol in yellow silky needles, almost insoluble in benzene and cold baryta-water, melting above 330° (626° F.); its solution in alkalies has a yellowish-red colour, but it does not colour mordants. It is converted into flavopurpurin by fusion with potassic hydrate. Its diacetyl derivative forms in pale yellow crystals melting at about 228° (442°·4 F.). By the addition of an excess of bromine to its alcoholic solution, anthraflavic acid is converted into a tetrabromoderivative, insoluble in all the ordinary menstrua.

Isoanthraflavic acid: $C_{14}H_6(OH)_2O_2$.—This dioxyanthraquinone also accompanies alizarin and anthraflavic acid in crude alizarin (Schunck and Roemer, *loc. cit.*), and is derived, like the latter, from an anthraquinonedisulphonic acid (Caro); being easily soluble in cold baryta-water, it is without difficulty separated from its isomerides. Isoanthraflavic acid crystallizes from aqueous alcohol in long yellow needles, which after drying over sulphuric acid retain a molecule of water; the anhydrous substance, like anthraflavic acid, does not melt at 330° (626° F.) but sublimes at a higher temperature. Its solutions in alkalies and in hot sulphuric acid are of a deep red colour, whereas the latter forms a yellow solution with anthraflavic acid; it is destitute of dyeing properties. By the action of potassic hydrate, it is converted into anthrapurpurin; with bromine it yields a tetrabromo-derivative moderately soluble in acetic acid; it does not furnish phthalic acid on oxidation with nitric acid. Its diacetyl-derivative forms pale yellow indistinct crystals which melt at about 195° (383° F.) (comp. Perkin, *Jour. Chem. Soc.*, 1876, i. 851).

Chrysazin: $C_{14}H_6(OH)_2O_2$.—To prepare this isomeride of alizarin, so-called chrysammic acid, $C_{14}H_2(NO_2)_4(OH)_2O_2$, obtained by the action of concentrated nitric acid on Barbadoes aloes, is converted into the corresponding amido-compound —the hydrochrysammid of Schunck—by reduction with a solution of sodic thiohydrate, and the diazo-compound resulting from the action of nitrous acid on the product decomposed by heating with alcohol. It crystallizes from acetic acid in red-brown glistening needles, melting at 191° (375°·8 F.); it dissolves in alkalies, forming a yellowish-red solution, which is not fluorescent, and which, on the addition of calcic and baric salts, yields red precipitates of the calcic and baric derivatives of chrysazin. It is destitute of dyeing properties. When distilled over zinc dust it yields anthracene. It is not converted into phthalic acid by oxidation with nitric acid. Diacetylchrysazin forms yellow crystals similar to those of benzoic acid, melting at 226°—230° (438°·8—446° F.). By heating chrysazin with an excess of fuming nitric acid in the water bath, it is converted into a tetranitrodioxyanthraquinone, which is in all respects identical with chrysammic acid from aloes (Liebermann, *loc. cit.*, p. 174).

Other isomerides of alizarin.—According to Schunck and Roemer, so-called anthraflavone contains, besides anthraflavic acid, a second isomeride of alizarin, distinguished by its solubility in benzene. It crystallizes in anhydrous needles, melting at 292° (557°·6 F.), and dissolves in alkalies forming a pure yellow-coloured solution.

Frangulic acid from frangulin (p. 694), according to Faust, is also an isomeride of alizarin; but it has been very insufficiently examined, and it is not improbable that it is a methylanthracene derivative (comp. Liebermann and Waldstein, *Deut. chem. Ges. Ber.*, ix. 1775).

Lastly, madder is said to contain an extremely small amount of an isomeride of alizarin, distinguished by dissolving in a solution of potassic or sodic hydrate with a blood-red colour, and by not yielding colours with alumina or iron mordants (Rochleder, *ibid.*, iii. 292).

(1706) TRIOXY-DERIVATIVES OF ANTHRAQUINONE; o–1 : 2 : 4 *Trioxyanthraquinone* or ***Purpurin:*** $C_{14}H_5(OH)_3O_2$.—Purpurin occurs together with alizarin in madder extract, being present, like the latter, in the fresh root as a glucoside; to separate it approximately from alizarin on the large scale, advantage is taken of the discovery of E. Kopp that the glucoside of purpurin is decomposed by warming with a solution of sulphurous acid to 50°—60° (122° —140° F.), whereas the glucoside of alizarin is only decomposed on heating to about 100° (212° F.). It may be further purified by dissolving it in boiling alum liquor, in which it is far more soluble than alizarin, adding acid to the filtered solution, and if necessary repeating the solution in alum liquor, &c.

after which it is several times re-crystallized from alcohol; or still better by extracting 'munjeet,' the root of *Rubia munjista*, with a boiling solution of aluminic sulphate, precipitating with hydrochloric acid and crystallizing the product from spirit. As munjeet does not contain alizarin, the purpurin is easily obtained in a pure state. The crude purpurin prepared by Kopp's method contains a considerable quantity of so-called pseudopurpurin, which Rosenstiehl, Plath and Liebermann (comp. *ibid.*, x. 1618) have shown to be a purpurincarboxylic acid, $C_{14}H_4(OH)_3O_2.COOH$. This substance is readily decomposed into purpurin and carbonic anhydride by heat or by boiling with potassic hydrate solution. Purpurin may be formed artificially from both alizarin and quinizarin by oxidation with manganic peroxide and sulphuric acid (De Lalande; Baeyer and Caro).

Purpurin crystallizes from aqueous alcohol in deep orange-coloured, thin, flattened prisms of the composition $C_{14}H_8O_5 + OH_2$; from strong alcohol it is deposited in dark-red anhydrous needles, melting at 253° (487°·4 F.), but it begins to sublime at 150° (302° F.). It dissolves in alkalies, producing deep red-coloured solutions; and on treatment with boiling baryta-water forms a purple lake quite insoluble in water; it dyes a red free from all blue tint with alumina mordants, and purples and blacks with ferric salts. Purpurin and alizarin are readily distinguished by means of the characteristic absorption spectra of their solutions in various menstrua; purpurin is also characterized by giving a pink fluorescent solution when dissolved in alum liquor. Its derivatives are obtained with less facility than those of alizarin, and it is a less stable body than alizarin; thus a solution of purpurin in alkali loses its colour on exposure to the air, becoming pale yellow in consequence of the oxidation of the purpurin. This behaviour renders it possible to detect traces of alizarin in presence of considerable quantities of purpurin, for if the latter be destroyed in this manner, the alizarin may then be easily recognized, as the products of oxidation of the purpurin do not affect its absorption spectrum. Purpurin, like alizarin, yields anthracene when distilled over heated zinc dust; when dissolved in alkali and heated with zinc, it is converted into pentoxyanthracene; and on oxidation with nitric acid, it yields phthalic acid. When heated with acetic anhydride at 180° (356° F.), it yields triacetylpurpurin, which crystallizes in yellow needles, melting at about 199° (390°·2 F.); on treatment with bromine it yields monobromopurpurin, which crystallizes in dark-red lustrous needles, melting at 276° (528°·8 F.) (comp. Schunck and Roemer, *Jour. Chem. Soc.*, 1877, i. 670).

Isopurpurin: $C_{14}H_5(OH)_3O_2$.—This isomeride of purpurin is produced in almost theoretical quantity on carefully heating isoanthraflavic acid with potassic hydrate. It crystallizes from acetic acid in minute orange-coloured anhydrous needles, melting above 330° (626° F.); its triacetyl-derivative crystallizes from acetic acid in pale yellow glistening scales, melting at about 221° (429°·8 F.). It yields a dibromo-derivative on treatment with bromine. Anthrapurpurin has about the same affinity for mordants as alizarin, and it yields analogous colours, but purer shades; the bands in its absorption spectrum are also in the same position as those of alizarin (Perkin, *Jour. Chem. Soc.*, xxvi. 425; Schunck and Roemer, *Deut. chem. Ges. Ber.*, ix. 678; x. 1821). Its dyeing properties are similar to those of purpurin. On treatment with bromine it yields a dibromo-derivative.

Flavopurpurin: $C_{14}H_5(OH)_3O_2$, isomeric with purpurin and isopurpurin, is formed by heating anthraflavic acid under pressure with a concentrated solution of potassic hydrate. It crystallizes from alcohol in golden-yellow anhydrous needles, melting above 330° (626°), but sublimes in long needles like alizarin. It dissolves in a solution of potassic hydrate forming a purple-coloured liquid, less red than that of purpurin but redder than that of isopurpurin, and which exhibits an extremely characteristic absorption spectrum. It forms a diacetyl-derivative, which crystallizes in golden-yellow plates, melting at 238° (460°·4 F.); or a triacetyl-derivative much more soluble in acetic acid, which crystallizes in sulphur-yellow needles, melting at 196° (384°·8 F.). Bromine converts it into a tribromo-derivative (Schunck and Roemer, *loc. cit.*; *ibid.*, x. 1821).

Oxychrysazin: $C_{14}H_5(OH)_3O_2$, is formed on fusion of chrysazin with potassic hydrate. It is somewhat difficultly soluble in alcohol; it dissolves in alkaline solutions with a violet colour, and yields colours with mordants intermediate in tint between those furnished by alizarin and purpurin. Its solution in alum liquor is not fluorescent like that of purpurin. Its triacetyl-derivative melts at about 193° (379°·4 F.) (Liebermann, *Ann. Chem. Pharm.*, clxxxiii. 191).

(?) o–1 : 2 : 3 *Trioxyanthraquinone* or *anthragallol:* $C_{14}H_5(OH)_3O_2$, formed by heating a mixture of benzoic and gallic acids, or of pyrogallol and phthalic anhydride, with sulphuric acid, sublimes in orange needles; it yields phthalic acid on oxidation. Its triacetyl-derivative forms pale yellow needles, melting at 171°—175° (339°·8—347° F.) (Seuberlach, *ibid.*, ix. 38).

(1707) TETROXY- AND HEXOXY-DERIVATIVES OF ANTHRAQUINONE; *Tetroxyanthraquinone; anthrachrysone:* $C_{14}H_4(OH)_4O_2$.—This compound is formed on heating dioxybenzoic acid from disulphobenzoic acid with concentrated sulphuric acid at 120°—140° (248°—284° F.). It forms yellow microscopic prisms, which do not melt even at 320° (608° F.); it dissolves in alkaline solutions and in sulphuric acid, forming red-coloured liquids, and it also dyes alumina mordants red. When passed over heated zinc dust it yields anthracene (Barth and Senhofer, *ibid.*, clxiv. 109).

By heating opianic acid, $C_6H_2(OCH_3)_2(COH).COOH$, with sulphuric acid, Liebermann and Chojnacki have obtained a red colouring matter, *rufiopin*, $C_{14}H_8O_6$, which apparently is also a tetroxyanthraquinone as it yields anthracene when passed over heated zinc dust. It crystallizes from alcohol in indistinct yellowish-red needles, and dissolves in alkaline solutions with a violet colour (*ibid.* clxii. 321).

Hexoxyanthraquinone; rufigallic acid: $C_{14}H_2(OH)_6O_2$.—This compound is formed on heating gallic acid with concentrated sulphuric acid, the conversion being complete at the temperature of the water bath; its formation in this manner is precisely analogous to that of anthrachrysone and anthraflavone from di- and monoxybenzoic acid respectively. It sublimes in yellowish-red transparent needles; it dissolves in sulphuric acid, forming a red solution; when moistened with a concentrated solution of potassic hydrate, it is coloured a magnificent indigo-blue, but with a more dilute solution it forms a violet-coloured liquid, from which, however, it is gradually deposited on standing. With alumina and iron mordants it yields colours similar to those of alizarin, but dull. When reduced by sodium amalgam, it yields a small quantity of alizarin; and by distillation over heated zinc dust it is converted into anthracene (comp. Jaffé, *Deut. chem. Ges. Ber.*, iii. 694; Klobukowski, *ibid.*, ix. 1056).

(1708) METHYLANTHRAQUINONE: $C_{15}H_{10}O_2 = CH_3.C_{14}H_7O_2$.—This homologue of anthraquinone is obtained by oxidation of methylanthracene (1394), and on further oxidation becomes converted into anthraquinonecarboxylic acid, $C_{14}H_7O_2.COOH$. It sublimes very readily in yellow needles, melting at 163° (325°·4 F.), easily soluble in boiling alcohol (Fischer, *ibid.*, viii. 675).

On converting methylanthraquinone into sulpho-acid, and fusing the potassic salt of the latter with potassic hydrate, it appears to yield *methylalizarin;* this substance forms red crystals melting at about 251° (483°·8 F.), and very closely resembles alizarin (Fischer).

Chrysophanic acid and emodin, two substances extracted from rhubarb, have ecently been shown by Liebermann and Fischer to be respectively the di- and rioxy-derivatives of methylanthraquinone (*Ann. Chem. Pharm.*, clxxxiii. 158);

chrysophanic acid has also been detected in the roots of several other species of *Rheum*, in several species of *Rumex*, and in yellow wall lichen (*Parmelia parietina*), and emodin in the bark of *Rhamnus frangula* (Liebermann and Waldstein, *Deut. chem. Ges. Ber.*, ix. 1775). Emodin and chrysophanic acid are distinguished by their behaviour with a solution of sodic carbonate, the former dissolving with a blood-red colour, the latter being insoluble. *Chrysophanic acid*, $CH_3.C_{14}H_5(OH)_2O_2$, crystallizes in golden-yellow needles, melting at 162° (323°·6 F.); it dissolves in solutions of alkalies with a cherry-red colour, and it yields red precipitates with lime and baryta-water, which, however, are decomposed by mere exposure to the air. Its diacetyl-derivative forms narrow glistening, pale yellow plates melting at about 203° (397°·4 F.). By dissolving it in fuming nitric acid it is converted into a tetranitro-derivative resembling that obtained from chrysazin. *Emodin*, $CH_3.C_{14}H_4(OH)_3O_2$, crystallizes from acetic acid in silky orange-red needles, melting at 245°—250° (473°—482° F.); its triacetyl-derivative, prepared by heating it with acetic anhydride at 180° (356° F.), melts at 190° (374° F.).

By oxidizing barbaloïn and socaloïn* with chromic acid mixture, Tilden has obtained a tetroxymethylanthraquinone, $CH_3.C_{14}H_3(OH)_4O_2$, which he terms *aloxanthin*, as an orange granular powder; it dissolves in sodic hydrate solution, forming a cherry-red coloured liquid, but has no affinity for mordants (*Jour. Chem. Soc.*, 1877, ii. 264).

(1709) DIMETHYLANTHRAQUINONE: $(CH_3)_2C_{14}H_6O_2$, formed by oxidation of dimethylanthracene, crystallizes in pale yellow needles, melting at 155°

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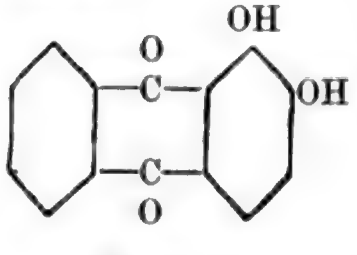
* The crystalline substances extracted from the various sorts of aloes differ somewhat in properties, but Tilden is inclined to regard them all as compounds of the formula $C_{16}H_{18}O_7$. Three varieties are usually distinguished: *Barbaloïn*, from Barbadoes aloes; *Zanaloïn*, from Zanzibar aloes, which is probably identical with *Socaloïn*, from Socatrine aloes, as so-called Zanzibar aloes is merely a highly crystalline variety of the drug imported from Socotra by way of Zanzibar; and *Nataloïn* from Natal aloes. Their principal characters are summarized in the following table (Tilden, *Trans. B. Pharm. Conf.*, 1875, 540; and *private communication*).

	BARBALÖIN. Anhydrous after drying in vacuo.	SOCALOÏN or ZANALOÏN Anhydrous after drying in vacuo.	NATALOÏN. Dried at 120° C.—130°.
Composition. $C_{16}H_{18}O_7$ requires C. 59·02 per cent. H. 5·59	C. 59·31 H. 5·88 (Stenhouse average) C. 59·23 H. 5·61 (Schmidt average)	C. 59·49 H. 5·80 (Tilden average) C. 59·2 H. 5·9 (Flückiger)	C. 59·56 H. 5·96 (Tilden average) C. 59·36 H. 6·10 (Flückiger average)
	Air dried crystals contain H_2O or $3H_2O$. (Assuming formula $C_{16}H_{18}O_7$)	Air dried crystals contain $3H_2O$	Crystals anhydrous
Melting point of anhydrous substance	About 150° (Stenhouse) 146°-148° (Schmidt)	118°-120° (Von Sommaruga)	180°-190°, Flückiger
Crystalline form	Minute orange-yellow prisms	Minute orange-yellow prisms	Greenish-yellow rectangular scales
When moistened with a drop of cold HNO_3 (S.G. 1·42)	Intense crimson colouration, fading quickly	Very slight change of colour	Blood-red colour, which does not fade; liquid dries up in the air to a red varnish
When boiled with nitric acid	Yields CO_2, trinitrophenol, oxalic, aloetic, and finally *chrysammic* acid	CO_2 &c., same as barbaloïn	CO_2, much oxalic acid, and a very little trinitrophenol. No chrysammic acid
Bichromate solution and sulphuric acid	Aloxanthin, besides CO_2 and a little acetic acid	Same as barbaloïn	CO_2 and much acetic acid, with traces of an odourous body not identified (qy. quinone)
On fusion with KOH		Acetic acid, paraoxybenzoic acid, α-orcin (Rochleder). Intermediate production of aloreinic acid, $C_6H_2(CH_3)_2(OH).COOH$ (Weselsky)? from Socotrine aloes	Acetic acid, paraoxybenzoic acid, and a body which gave the qualitative reactions of β-orcin. It may, however, have been Weselsky's acid.

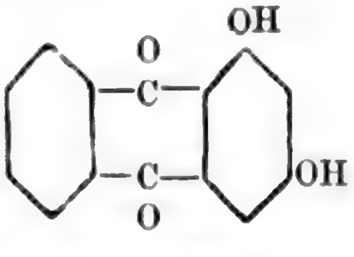
(311° F.); on oxidation it yields methylanthraquinonecarboxylic acid, $CH_3.C_{14}H_6O_2COOH$, and anthraquinonedicarboxylic acid, $C_{14}H_6O_2(COOH)_2$ (Wachendorff and Zincke, *ibid.*, x. 1481).

By heating carmine red from cochineal with sulphuric acid, Liebermann and Dorp (*Ann. Chem. Pharm.*, clxiii. 105) have obtained a red colouring matter, ***ruficocein***, $C_{16}H_{10}O_6$, which apparently is an oxyquinone-derivative related to dimethylanthracene.

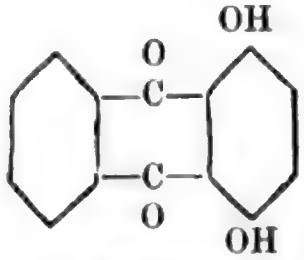
(1710) CONSTITUTION OF ANTHRAQUINONE AND ITS OXY-DERIVATIVES.—The formation of anthraquinone from phthalic chloride and benzene, and of oxyanthraquinones from phthalic anhydride and oxy-derivatives of benzene, leaves no doubt as to the correctness of the formula $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}C_6H_4$ for anthraquinone (comp. 1389). The production of alizarin and quinizarin from catechol and quinol respectively suffices not only to indicate that the OH groups in these compounds are both present in the same C_6 group—which is confirmed by their yielding phthalic acid on oxidation—but also affords evidence of the relative positions of these groups (*vid.* p. 376); and since purpurin is formed on oxidation of both alizarin and quinizarin, it must also be supposed that the OH groups in this modification of trioxyanthraquinone are all in the same C_6 group, a conclusion which necessarily extends to purpuroxanthin, the dioxyanthraquinone formed by reduction of purpurin, and which is in harmony with the observation that purpurin and purpuroxanthin both furnish phthalic acid on oxidation. Inasmuch, however, as only three dioxyanthraquinones are possible in which the OH groups are in the same C_6 group, and the constitution of two of these is known, that of the third is at once determined; so that alizarin, purpuroxanthin, and quinizarin may be represented by the following symbols:



Alizarin.



Purpuroxanthin.



Quinizarin.

The formula assigned to anthraquinone admits of the existence of only two monoxyanthraquinones, one having the OH group in the position 1,* the other the OH group in the position 2. Inasmuch as oxyanthraquinone may be

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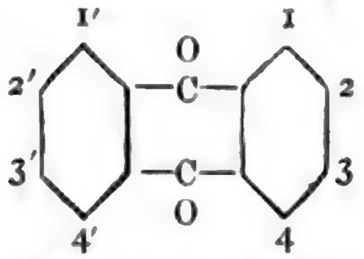
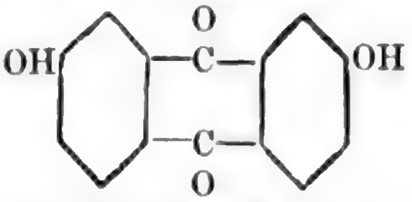
* If it be agreed to represent anthraquinone by the symbol

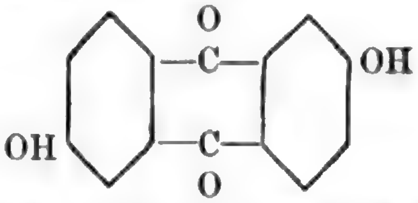


and to number the "positions" in the manner shown, the constitution of anthraquinone-derivatives may be very simply indicated by figures as in the case of benzene-derivatives; if the displacing radicles are supposed to be contained only in the one C_6 group, this may be shown as in the case of alizarin, for example, by the symbol o–1 : 2, whereas the isomeride containing an OH group in the position 1 in the one C_6 group and in the position 2 in the other would be represented by the symbol 1–2′ or, which is the same thing, 1′–2.

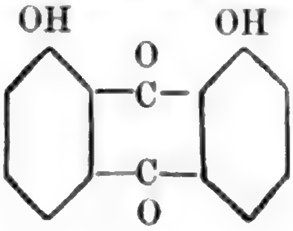
obtained from anthraquinonesulphonic acid, and it is the tendency of sulphuric acid chiefly to form meta-derivatives, it appears probable that this compound is a meta-derivative, and therefore that the OH group in erythoxyanthraquinone is in the position 1; the fact that erythoxyanthraquinone is more highly coloured lends some support to this conclusion, for meta-derivatives, as a rule, do not appear to furnish colouring matters.

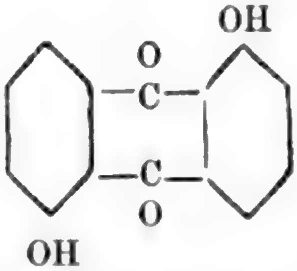
Few data exist from which the constitution of the remaining dioxy-derivatives of anthraquinone may be deduced. The formation of anthraflavic acid from metaoxybenzoic acid necessitates the assumption that the OH groups are in different C_6 groups, in which each must occupy the meta-position, and two formulæ are therefore possible—viz., 2′—2 and 3′—2; thus:





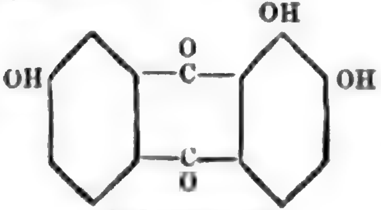
The isomeride which, according to Schunck and Roemer, is formed together with anthraflavic acid, would be represented by whichever of these formulæ does not belong to the latter. The fact that no phthalic acid is formed on oxidation of isoanthraflavic acid indicates that the OH groups in it are in different C_6 groups, but there is no further evidence extant which would serve to throw light on its constitution. Chrysazin also does not furnish phthalic acid, and from the great readiness with which this body yields a tetranitro-derivative, it appears probable that both OH groups occupy ortho-positions, and therefore that it may be represented by one of the two formulæ:



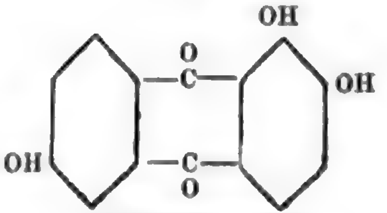


It is a remarkable fact that none of the dioxyanthraquinones in which the OH groups are in different C_6 groups exhibit any affinity for mordants, and this apparently is also the case with the monoxyanthraquinones and with purpuroxanthin, in which the OH groups are relatively in the meta-position; only alizarin and quinizarin, in which respectively the OH groups are relatively in the positions 1 : 2 and 1 : 4 act as dyes.

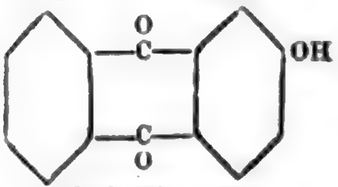
Purpurin is shown by its formation from alizarin and quinizarin to have the three OH groups in the one C_6 group and in the relative positions 1 : 2 : 4. Anthragallol from the manner in which it is formed also contains the three OH groups in the one C_6 group, and these must be supposed to occupy relatively the positions 1 : 2 : 3. Positive data, which would enable us to infer the constitution of the remaining trioxanthraquinones, are wanting; but as they are all colouring matters, and closely resemble alizarin, it appears probable that they are related to the latter somewhat in the manner represented by the following symbols:



(?) Isopurpurin.



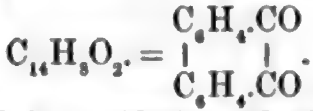
(?) Flavopurpurin.

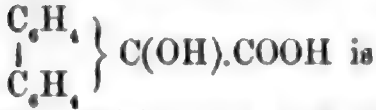
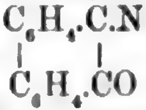


(?) Oxychrysazin.

From the manner in which they are formed, anthrachrysone and rufigallic acid doubtless contain respectively two and three OH groups in each C_6 group, but their relative positions are doubtful, as the constitution of the acids from which they are derived is not yet satisfactorily ascertained; probably, however, the OH groups in the latter are contiguous as in anthragallol.

Methylanthraquinone probably has the CH_3 group in the position 3 as the ditolylmethane from which methylanthracene is obtained is doubtless a para-derivative of benzene; moreover, the anthraquinonecarboxylic acid formed by its oxidation appears to be identical with that prepared from anthraquinone-sulphonic acid, which in all probability is a meta-derivative of anthraquinone.

(1711) **Phenanthraquinone**: $C_{14}H_8O_2$. =  $\begin{matrix} C_6H_4.CO \\ | \quad\quad | \\ C_6H_4.CO \end{matrix}$. This quinone, isomeric with anthraquinone, is formed by oxidation of phenanthrene (comp. p. 378). It is sparingly soluble in hot water, but freely dissolves in benzene and acetic acid, and crystallizes in dark, reddish-yellow or orange-yellow prisms; it melts at 198° (388°·4 F.), and sublimes at a higher temperature in orange-red plates.

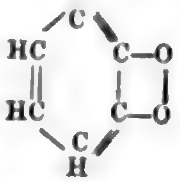
Phenanthraquinone is distinguished from anthraquinone by a variety of reactions. Thus it combines with acid sulphites, forming crystalline compounds such as that with sodic hydric sulphite, $C_{14}H_8O_2.NaHSO_3 + 2OH_2$. It is converted into the corresponding quinol (p. 537) by the action of an aqueous solution of sulphurous acid at 100° (212° F.); and phenanthraquinol yields the corresponding quinhydrone on careful oxidation. It is not converted into a sulpho-acid by the action of sulphuric acid at 100° (212° F.), and on heating more strongly is decomposed; it may, however, be converted into sulpho-acids by means of sulphuric anhydride. No colouring matters derived from it are known. By oxidation with chromic acid, it is readily converted into diphenic acid, $C_6H_4(COOH).C_6H_4(COOH)$. When heated with soda-lime, it yields diphenyl, $C_6H_5.C_6H_5$, but if heated with burnt lime, it is converted into diphenylene ketone (p. 1686). By prolonged boiling with a concentrated alcoholic solution of potassic hydrate, it is converted into diphenic acid; if, however, an aqueous solution of sodic hydrate is employed, *diphenyleneglycolic acid*  $\left.\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\right\} C(OH).COOH$ is produced, an isomeric change taking place similar to that which occurs in the formation of diphenylglycolic acid from benzil (p. 787). On heating phenanthraquinone with an alcoholic solution of ammonia, *phenanthrimidoquinone*,  $\begin{matrix} C_6H_4.C.NH \\ | \quad\quad | \\ C_6H_4.CO \end{matrix}$, is obtained; it forms long yellow needles, melting at 147° (296°·6 F.); hydrochloric acid reconverts this compound into the quinone. On treatment with bromine, and on nitration, phenanthraquinone yields bromo- and nitro-derivatives, although by no means readily (Fittig and Ostermayer, *Ann. Chem. Pharm.*, clxvi. 365; Graebe, *ibid.*, clxvii. 139; Hayduck, clxvii. 184; Ostermayer, *Deut. chem. Ges. Ber.*, vii. 1089; Anschütz and Schulz, *ibid.*, ix. 1400; x. 21, 323; Friedlaender, *ibid.*, x. 534).

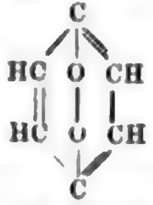
(1712) **Pyrenequinone**: $C_{16}H_{18}O_2$, obtained by oxidation of pyrene (1399), resembles anthraquinone in its properties; it crystallizes from acetic acid in red needles or prisms. When boiled with a solution of potassic hydrate and zinc dust, it dissolves, forming a red liquid from which it is again deposited on exposure to the air; cold sulphuric acid dissolves it, forming a brown-coloured liquid (Graebe).

(1713) **Dioxyretistene**: $C_{16}H_{14}O_2$.—This compound, formed by oxidation of the hydrocarbon retene (1396), is apparently a quinone, as it dissolves, although with difficulty, in a solution of hydric sodic sulphite, and also when heated with potassic hydrate solution and zinc dust. It crystallizes from alcohol in dark orange-coloured flat prisms, melting at about 190° (374° F.); according to Ekstrand, it does not yield the hydrocarbon $C_{18}H_{14}$ when distilled with zinc dust (*Ann. Chem. Pharm.*, clxxxv. 98).

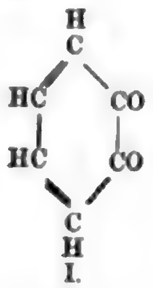
(1714) CHRYSOQUINONE: $C_{18}H_{10}O_2$, obtained in a similar manner from chrysene (1405), crystallizes from benzene in reddish-yellow needles, melting at about 220° (428° F.); it dissolves in concentrated sulphuric acid, forming a beautiful blue-coloured solution, from which water precipitates the unaltered substance (Liebermann). Like phenanthraquinone, it is converted into the corresponding quinol by digestion with a solution of sulphurous acid at 100° (212° F.); it forms crystalline compounds with the acid sulphites, and enters into reaction with ammonia; when distilled with soda-lime it yields the hydrocarbon $C_{16}H_{12}$ (Graebe, *Deut. chem. Ges. Ber.*, vii. 782).

(1715) CONSTITUTION OF THE QUINONES.—The constitution of benzoquinone and of the quinones having similar properties is still open to discussion, that of anthraquinone and phenanthraquinone and the allied quinones having alone been satisfactorily established. According to the hypothesis advanced by Graebe, and which is that which has obtained most general credence, the quinones are formed by the displacement of 2 atoms of hydrogen by 2 atoms of oxygen, which together act as a dyad radicle in consequence of their being united by an affinity of each. Graebe made the somewhat arbitrary assumption that the oxygen atoms became attached to contiguous carbon atoms, as only one of the dihydroxy-derivatives of benzene was convertible into quinone; but it is now placed beyond doubt, however, that quinol and all the di-derivatives of benzene which furnish quinone* are not ortho- or 1 : 2 derivatives but para- or 1 : 4 derivatives, and therefore quinone is represented by the second of the following symbols, the first being that originally proposed by Graebe:





The alternative hypothesis which has been entertained of late is that the quinones are all di-ketones; that is to say, that they contain the group CO twice. The formation of a di-ketone of the composition of quinone from benzene, however, cannot be expressed with the aid of Kekulé's benzene symbol, as it necessitates the partial disunion of two of the carbon atoms which are united by two affinities of each, and this could only take place if quinone were an ortho-compound (fig. I.); but it may be represented by means of the so-called prism symbol—thus:



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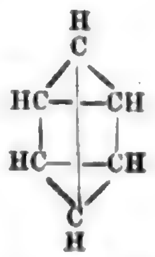
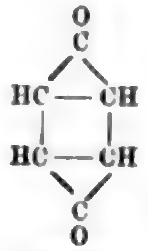


Benzene.†



Quinone.

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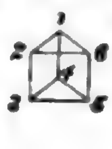
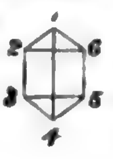
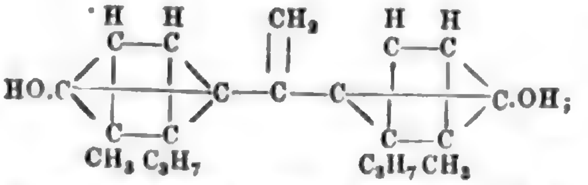
* The β-naphthaquinone of Stenhouse and Groves must be either an ortho- or meta-derivative, however.

† Benzene may be represented simply by a prism instead of by this complicated symbol, thus 

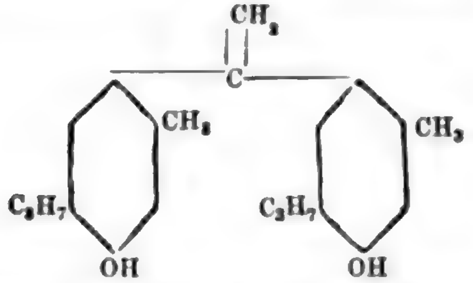
or thus 

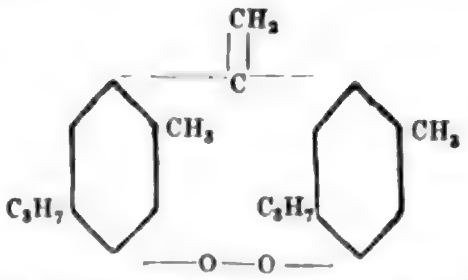
. This symbol is the only one besides Kekulé's by which the "constitution" of the various derivatives of benzene can be satisfactorily represented, and in some respects it has an advantage over it. Thus

There is only one instance in which this hypothesis appears to be inadmissible—viz., in explanation of the production of a quinone of the formula $C_{22}H_{28}O_2$ from the compound $CH_2{=}C(C_{10}H_{12}.OH)_2$ obtained by reduction of the product of the reaction of chloral hydrate on thymol (1701). As this compound is a para-derivative—the parent compound yields cymoquinone on oxidation—it is impossible to account for its conversion into a ketone in a satisfactory manner by means of the prism symbol, as may be seen by reference to the following figure:



but the formation of a quinone from such a compound is readily expressed in accordance with Graebe's hypothesis—thus:





The evidence at present at our disposal, however, is scarcely sufficient to warrant the rejection or adoption of either view. Graebe's hypothesis, although serving well to explain the properties of benzoquinone and its homologues, involves the assumption that the oxygen atoms are united in a manner altogether without analogy, at least in the case of carbon compounds, and on this ground alone it is open to question unless it can be shown that the ketone hypothesis does not equally well accord with their behaviour. Moreover, although benzoquinone and its homologues differ greatly in their properties from anthraquinone, which is generally admitted to be a di-ketone, they in many respects resemble phenanthraquinone, which undoubtedly is also a di-ketone, and the difference between these quinones is certainly no greater than between many closely allied ketones, such as methylethyl ketone and methylphenyl ketone, for example, only the first of which is capable of combining with acid sulphites.

From these remarks it will be evident that the determination of the constitution of benzoquinone and its homologues is a problem of considerable interest, especially as the acceptance of the one hypothesis would involve the rejection of Kekulé's benzene symbol.

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it indicates the existence of only 3 di-derivatives—viz., of a meta-derivative (1 : 2 or 1 : 6), of an ortho-derivative (1 : 3 or 1 : 5), and of a para-derivative (1 : 4); and it is possible to represent the formation of metabromobenzoic and isophthalic acids by oxidation of the compounds resulting from the action of zincic ethide on benzene dibromide, $C_6H_6Br_2$, which cannot be accounted for by means of Kekulé's symbol (comp. foot-note, p. 395). Obviously, whereas Kekulé's symbol represents the radicles in the ortho-di-derivatives as associated with contiguous carbon atoms, this symbol represents them as associated with carbon atoms which are not united: so that the term relative position of such and such radicles has reference merely to a given symbol and has no absolute meaning whatever. The constitution of the derivatives of benzene and of allied hydrocarbons may, however, be expressed in accordance with the present theory entirely without reference to the constitution of benzene itself by means of the simple hexagon symbol so frequently employed in these pages.

§ V. SULPHINES AND SULPHONES.

These compounds bear a similar relation to sulphurous and sulphuric acid respectively that the ketones bear to carbonic acid, thus:

$CO(OH)_2$ Carbonic acid.	$SO(OH)_2$ Sulphurous acid.	$SO_2(OH)_2$ Sulphuric acid.
$CO(C_2H_5)_2$ Diethylketone.	$SO(C_2H_5)_2$ Diethylsulphine.	$SO_2(C_6H_5)_2$ Diphenylsulphone.

The resemblance extends, however, only to their formulæ, and not to their properties.

The sulphines are obtained by oxidation of the corresponding thioethers, and have hitherto only been prepared from those of the $S(C_nH_{2n+1})_2$ series. The sulphones are formed in a similar manner, and by the action of sulphuric acid and of chlorhydric sulphate, $ClSO_2.OH$, on hydrocarbons such as benzene and naphthalene. The sulphones resist oxidation, but they are readily reconverted into thioethers by the action of reducing agents.

(1716) DIMETHYLSULPHINE: $SO(CH_3)_2$.—Nitric acid acts with great violence on methylic sulphide, $S(CH_3)_2$; if, however, the sulphide be gradually dropped into the well-cooled acid it dissolves, and on evaporating the solution on the water bath, a residue is finally obtained which solidifies on cooling to a mass of colourless crystals of the nitrate $S(CH_3)_2(OH).NO_3$. By decomposing a solution of this compound with baric carbonate, a solution of the oxide $SO(CH_3)_2$ (or ? of the hydrate $(CH_3)_2S(OH)_2$) is obtained, from which the latter may be isolated by evaporating the liquid at first in the water bath and then in vacuo, and extracting with alcohol or ether. Dimethylsulphine is a colourless, odourless, oily liquid, which, on cooling by a refrigerating mixture, solidifies to a mass of crystals; it decomposes on distillation, and on treatment with zinc and sulphuric acid it is reduced to methylic sulphide.

Methylethylsulphine, $CH_3.SO.C_2H_5$, *diethylsulphine*, $SO(C_2H_5)_2$, *dibutylsulphine*, $SO(C_4H_9)_2{}^{a}$, *diisobutylsulphine*, $SO(CH_2.C_3H_7{}^{\beta})_2$, *ethylisoprimary-amylsulphine*, $C_2H_5.SO.CH_2.CH_2.C_3H_7{}^{\beta}$, and *diisoprimary-amylsulphine*, $SO(CH_2.CH_2.C_3H_7{}^{\beta})_2$, have been prepared in a similar manner by oxidizing the corresponding thioethers with nitric acid; they closely resemble the methyl compound in their properties (comp. Saytzeff, *Ann. Chem. Pharm.*, cxxxix. 354; cxliv. 148; Grabowsky, *ibid.*, clxxv. 348; Claessen, *Jour. pr. Chem.* [2], xv. 174).

(1717) PHENYLDISULPHINE: $C_{12}H_{10}S_2O_2 = C_6H_5.OS.SO.C_6H_5$, the analogue of the ketone *dibenzoyl* or *benzil* (p. 787), is formed in small quantity on oxidation of thiophenol, being doubtless derived from the disulphide $C_6H_5.S.S.C_6H_5$, which is the first product of oxidation; it is also obtained together with benzenesulphonic acid on heating benzenesulphinic acid with water: $3C_6H_5.SO_2H = (C_6H_5)_2S_2O_2 + C_6H_5.SO_3H + OH_2$ (Otto, *Deut. chem. Ges. Ber.*, ix. 1639). It crystallizes from alcohol in transparent monoclinic plates, melting at 45° (113° F.); on oxidation it is converted into benzenesulphonic acid, and on reduction into thiophenol; when boiled with potassic hydrate solution it yields benzenesulphonic and benzenesulphinic acids and phenylic disulphide. The homologous compound, *paratolyldisulphine*, is formed in a similar manner from thioparacresol.

(1718) DIMETHYLSULPHONE: $(CH_3)_2SO_2$.—To prepare this compound from dimethylsulphine, it is necessary to heat the latter with concentrated nitric acid at 100° (212° F.). It forms colourless prisms easily soluble in water and alcohol, melting at 109° (228°·2 F.), and boils without decomposition at 238° (460°·4 F.); it does not combine with acids like dimethylsulphine (Saytzeff, *loc. cit.*). *Diethylsulphone*, $(S_2H_5)_2SO_2$, and *dibutylsulphone*, $(C_4H_9)_2SO_2$, are in all respects similar compounds (Oefele, *Ann. Chem. Pharm.*, cxxxii. 86; Grabowski, *loc. cit.*); the former melts at 70° (158° F.) and boils at 248° (478°·4 F.); the latter melts at 43°·5 (110°·2 F.)

(1719) DIPHENYLSULPHONE or *sulphobenzid:* $(C_6H_5)_2SO_2$, is obtained by oxidation of phenylic sulphide $(C_6H_5)_2S$, and by the action of sulphuric anhydride, sulphuric chlorhydrate and pyrosulphuric acid on benzene. It crystallizes from alcohol in rhombic plates, melting at 126° (258°·8 F.) It dissolves in hot concentrated sulphuric acid, being converted into benzenesulphonic acid, but is not in the least acted upon by an alcoholic solution of potassic hydrate even at 180° (356° F.). If dissolved in carbonic bisulphide, it is not attacked by chlorine either in shade or sunshine, even in presence of iodine, but if heated to its melting point, it is resolved into chlorobenzene and benzenesulphonic chloride, $SO_2(C_6H_5)_2 + Cl_2 = C_6H_5Cl + C_6H_5.SO_2Cl$ (Otto and Gruber, *Ann. Chem. Pharm.*, cxlix. 174). It is said to yield a liquid dichlorinated derivative when acted on by iodine chloride at 100° (212° F.); an isomeric crystalline *dichlorophenylsulphone*, $(C_6H_4Cl)_2SO_2$, melting at 141° (285°·8 F.), is obtained by the action of sulphuric anhydride on chlorobenzene; the latter may be also prepared by the action of sulphuric chlorhydrate, and by means of this reagent corresponding bodies are formed from bromo- and iodobenzene (Armstrong).

By heating phenol with half its weight of fuming sulphuric acid at 180°—190° (356°—374° F.), it is converted into *paradioxyphenylsulphone* or *oxysulphobenzid*, $SO_2(C_6H_4.OH)_2$, a number of derivatives of which have been described by Glutz and Annaheim (*Jour. pr. Chem.* [2], i. 14; ii. 385; *Ann. Chem. Pharm.*, clxxii. 28; *Deut. chem. Ges. Ber.*, vii. 436). This compound forms glistening prismatic needles, melting at 239° (462°·2 F.); it dissolves in alkaline carbonates, but the resulting metallic derivatives are formed by the displacement of only a single atom of hydrogen; when heated with sulphuric acid, it yields phenolparasulphonic acid.

By the action of sulphuric anhydride, toluene is converted into *ditolylsulphone*, $SO_2(C_6H_4.CH_3)$, a crystalline body which melts at about 156° (312°·8 F.) (Otho and Gruber). This is the only homologue of diphenylsulphone at present known.

By heating a mixture of naphthalene and benzenesulphonic chloride with zinc, Chrustschoff has obtained a crystalline *phenylnaphthylsulphone*, $C_6H_5.SO_2.C_{10}H_7$, melting at 121° (249°·8 F.) (*Deut. chem. Ges. Ber.*, vii. 1167).

According to Stenhouse and Groves (*ibid.*, ix. 682), two isomeric *naphthylsulphones*, $SO_2(C_{10}H_7)_2$, are formed simultaneously on heating naphthalene with sulphuric acid; they melt respectively at 123° (253°·4 F.) and 177° (350°·6 F.).

CHAPTER X.

THE ACIDS AND THEIR MORE IMMEDIATE DERIVATIVES.

§ I. *Acids of the $C_nH_{2n+1}.COOH$ or acetic series;*—§ II. *Amido- and oxy-acids derived from the acids of the acetic series. Carbonic acid. Acids of the lactic series;*—§ III. *Acids of the $C_nH_{2n}(COOH)_2$ or succinic series;*—§ IV. *Amido- and oxy-acids derived from the acids of the succinic series. Malic and tartaric acids;*—§ V. *Polybasic acids of other series derived from the paraffins. Citric acid;*—§ VI. *Acids of the $C_nH_{2n-1}.COOH$ or acrylic series;*—§ VII. *Acids of the $C_nH_{2n-2}(COOH)_2$ or fumaric series;*—§ VIII. *Acids of the $C_nH_{2n-3}.COOH$ series;*—§ IX. *Acids of the $C_nH_{2n-7}.COOH$ or benzoic series;*—§ X. *Amido- and oxy-acids derived from the acids of the benzoic series;*—§ XI. *Acids of the $C_nH_{2n-8}(COOH)_2$ or phthalic series;*—§ XII. *Polybasic acids of other series derived from hydrocarbons of the benzene series;*—§ XIII. *Acids of the $C_nH_{2n-9}.COOH$ or cinnamic series;*—§ XIV. *Acids of other series;*—§ XV. *Unclassified acids;*—§ XVI. *Sulphinic and sulphonic acids.*

UNTIL recently it has been the practice to apply the term acid almost indiscriminately to all compounds furnishing metallic derivatives when acted upon by metallic hydroxides or hydrates, or by metallic carbonates, so that bodies of the most various classes, often having no other properties in common, and bearing the most distant relation to each other, have thus been classed together. On carefully comparing the compounds which exhibit "acid properties," that is to say, which contain one or more atoms of hydrogen displaceable by metals, it becomes evident that in all cases the hydrogen is associated with a radicle containing a more or less negative element, such as one of the halogens, oxygen, sulphur, or nitrogen; so that, in fact, all compounds of hydrogen with negative radicles manifest acid properties. Thus, even the alcohols of the $C_nH_{2n+1}.OH$ series, in which one of the atoms of hydrogen is associated with a feebly negative radicle of the form $C_nH_{2n+1}O$ (negative only by reason of the presence of oxygen, the C_nH_{2n+1} radicles being strongly positive), yield metallic derivatives when submitted to the action of the hydroxides of the alkali metals; the alcohols of the $C_nH_{2n-7}.OH$ series, far more readily furnish metallic derivatives, which, moreover, are much more stable than those derived from the alcohols of the $C_nH_{2n+1}.OH$ series, the radicle associated with hydrogen in these compounds being more negative than the $C_nH_{2n+1}O$ radicle, as the radicles of the C_nH_{2n-7} series are in a marked degree negative in comparison with those of the C_nH_{2n+1} series. Also, by introducing negative radicles such as NO_2 in place of hydrogen, compounds destitute of acid properties, or feebly acid bodies, often have acid properties conferred upon them, or become more strongly acid; instances in point are the nitro-paraffins (1202) and the nitro-derivatives of phenol (1467).

On this account, chemists have been led in the case of carbon compounds to narrow the definition of the term acid, and to apply it only to bodies in which one or more atoms of hydrogen are rendered displaceable by metals by virtue of the presence in the compound of negative radicles of a particular kind. What may be termed organic acids proper are now almost universally regarded as compounds containing the group COOH, the hydrogen in this group being that which is displaced by metals in the formation of true salts. These carboxylic or carbo-acids, as they are most usually termed, may also be regarded as derivatives of carbonic acid, $CO(OH)_2$: viz., as formed from it by the displacement of one of the OH groups in a single molecule by a monad radicle—in which case a monobasic acid results, or by the displacement of *n*-OH groups in *n* molecules by an *n*-valent radicle, whereby a polybasic (*n*-basic) acid is formed. The term acid is further applied to compounds bearing a similar relation to the polybasic acids formed from negative elements other than carbon, such as sulphuric acid, phosphoric acid, &c.

(1720) *Methods of formation.*—A large number of carboxylic acids are products of special reactions, or are derived from special sources, but the following are general reactions by which many of them are formed:—1. By oxidation of hydrocarbons. The paraffins and, in fact, all hydrocarbons in which the carbon atoms may be regarded as associated together in such manner that they form an open chain, do not appear to furnish acids on oxidation bearing any simple relation to themselves; the hydrocarbons of the benzene series, however, and those similar to them in constitution, behave in a very definite manner, the side chain or chains, whatever their nature, being ultimately oxidized to carboxyl (comp. 1295).

2. By oxidation of aldehydes. It has already been pointed out that the aldehydes are very readily converted by oxidation into corresponding acids. The reaction may be represented as one of double decomposition; thus:

$$\underset{\text{Aldehyde.}}{R'.COH} + (O + OH_2) = \underset{\text{Acid.}}{R'.COOH} + OH_2.$$

The primary carbinols, which yield aldehydes on oxidation, may of course be converted into corresponding acids by continued oxidation. The behaviour of secondary and tertiary carbinols and of phenols, which do not yield corresponding acids on oxidation, has already been discussed.

3. By displacing one or more atoms of hydrogen in hydrocarbons by carboxyl. To effect this the haloid derivative of the hydrocarbon is first prepared, and is converted into the corresponding cyano-derivative by double decomposition with a metallic cyanide, and the cyano-derivative is then heated with water and hydrochloric or sulphuric acid or an alkali. For example:

$$\underset{\text{Methane.}}{CH_4} + Cl_2 = \underset{\text{Chloromethane}}{CH_3Cl} + HCl; \ \underset{\text{Chloromethane.}}{CH_3Cl} + KCN = \underset{\text{Cyanomethane.}}{CH_3.CN} + KCl;$$
$$\underset{\text{Cyanomethane.}}{CH_3.CN} + 2OH_2 + HCl = \underset{\text{Acetic acid.}}{CH_3.COOH} + NH_4Cl.$$

It is the practice in most cases to decompose the cyanides with the aid of an alkali, but it would appear that in many cases slightly diluted sulphuric acid may be advantageously employed; thus by heating cyanethane, $C_2H_5.CN$, at 100° (212° F.) with a mixture of 3 vols. sulphuric acid and 2 vols. water, almost pure propionic acid, $C_2H_5.COOH$, is produced (Beckurt and Otto, *Deut. chem. Ges. Ber.*, x. 262).

By employing the haloid hydrocarbon derivatives obtained by the action of haloid acids or of haloid phosphorus compounds on the alcohols, acids may be obtained formed from the alcohols by the displacement of the OH group by the group COOH. The haloid derivatives available for the purpose are only those in which the halogen is associated with a carbon atom, or with carbon atoms, forming part of an open chain, and even these do not always furnish acids, but sometimes resist the action of cyanides, and at others are acted upon in a different manner. To prepare acids from hydrocarbons such as benzene, the hydrocarbon is converted into a sulphonic acid by treatment with sulphuric acid, and a salt of this acid is distilled with a cyanide, the resulting cyanide being then decomposed in the manner stated; thus:

$$\underset{\text{Benzene.}}{C_6H_6} + SO_4H_2 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5.SO_3H} + OH_2; \ C_6H_5.SO_3K + KCN = \underset{\text{Cyanobenzene.}}{C_6H_5.CN} + K_2SO_3;$$
$$\underset{\text{Cyanobenzene.}}{C_6H_5.CN} + 2OH_2 + HCl = \underset{\text{Benzoic acid.}}{C_6H_5COOH} + NH_4Cl.$$

(1721) *General properties.*—The carboxylic acids readily enter into reaction with metallic oxides, hydroxides and carbonates forming *metallic salts*, the hydrogen of the group COOH being displaced by an equivalent amount of metal. In polybasic acids, the several atoms of hydrogen of the several COOH groups may be displaced one by one, and from each acid one or more *acid salts* may be obtained, as well as a *normal salt*, an acid which is *n*-basic yielding $n-1$ acid salts. Some monobasic acids also furnish *hyperacid salts* of the form R′.COOM′.R′.COOH.

The acids also enter into reaction with the alcohols in precisely the same manner as with metallic hydroxides, forming *acid*, *normal* and *basic ethereal salts*; the basic ethereal salts are the analogues of the basic metallic salts derived from polyhydric metallic hydroxides, being formed by the partial displacement of the OH groups in polyhydric alcohols by radicles resulting from the acids by the withdrawal of the hydrogen atoms of the COOH groups.

The acids are not affected by the haloid acids, but when submitted to the action of the haloid phosphorus compounds, they yield *acid halides—acid chlorides*, *bromides* and *iodides*, the group OH in the COOH group being displaced by chlorine, bromine or iodine. These compounds are very readily reconverted into the acids by decomposition with water.

By the action of heat on their ammonic salts, or by treating their ethereal salts and acid halides with ammonia, the acids are converted into *amic acids* and *acid amides*, the amic acids being formed by the displacement of part, and the acid amides by the displacement of the whole, of the OH groups in the COOH groups present in the acid. These compounds are also readily decomposed by water.

By the action of the acid chlorides of monobasic acids on metallic salts of the same acids, *acid anhydrides* are formed, which are related to the acids in the same way that the ethers are to the alcohols; thus:

$$\underset{\text{Monobasic acid.}}{\mathrm{R'.COOH}} \qquad \underset{\text{Acid anhydride.}}{\mathrm{(R.COO)_2O}} \qquad \underset{\text{Monohydric alcohol.}}{\mathrm{R'.OH}} \qquad \underset{\text{Ether.}}{\mathrm{(R'.O)_2O.}}$$

Many polybasic acids furnish corresponding compounds. The acid anhydrides are as a rule readily decomposed by water.

The COOH group in acids may often be displaced by hydrogen, by distilling their baric or calcic salts with baric or calcic hydrate; for example, benzene is obtained on distilling calcic benzoate with calcic hydrate:

$$\underset{\text{Calcic benzoate.}}{\mathrm{(C_6H_5.CO_2)_2Ca}} + \mathrm{Ca(OH)_2} = \underset{\text{Benzene.}}{\mathrm{2C_6H_6}} + \mathrm{2CaCO_3.}$$

The formation of ketones by heating metallic salts of acids has been previously described.

§ I. Acids of the C_nH_{2n+1}.COOH or Acetic Series.

(1722) The following acids of this series are known:

			M.P.	B.P. °C.
CH_2O_2	Formic acid	H.COOH	8·5	100
$C_2H_4O_2$	Acetic acid	CH_3.COOH	16·7	118
$C_3H_6O_2$	Propionic or methacetic acid	C_2H_5.COOH	liq. at -21	140·7
$C_4H_8O_2$	Butyric or ethacetic acid	$C_2H_5.CH_2$.COOH	0°	162·4
	Isobutyric or dimethacetic acid	$(CH_3)_2$.CH.COOH	—	154
$C_5H_{10}O_2$	Pentylic (valeric) or propacetic acid	$C_3H_7^{\alpha}.CH_2$.COOH	liq. at –16	185
	Isopentylic or isopropacetic acid	$(CH_3)_2CH.CH_2$.COOH	—	175
	Methethacetic acid . .	$C_2H_5.CH(CH_3)$.COOH	—	173
	Trimethacetic acid . .	$C(CH_3)_3$.COOH	35·4	163·8
$C_6H_{12}O_2$	Hexylic (caproic) or tetrylacetic acid . .	$C_4H_9^{\alpha}$.COOH	–2	205
	Isohexylic or isoprimary-tetrylacetic acid . .	$C_4H_9^{\beta}$.COOH	liq. at –18	200
	Diethacetic acid . . .	$CH(C_2H_5)_2$.COOH	—	196
	Dimethethacetic acid .	$C_2H_5.C(CH_3)_2$.COOH	–14	187
$C_7H_{14}O_2$	Normal heptylic or œnanthylic acid	$C_6H_{13}^{\alpha}$.COOH	–10·5	224
$C_8H_{16}O_2$	Normal octylic or caprylic acid	$C_7H_{15\alpha}$.COOH	16·5	236
	Isosecondary octylic acid.	$\underset{\text{COOH}}{\underset{\mid}{CH}}(CH_3).CH_2.C(CH_3)_3$	—	abt. 215
$C_9H_{18}O_2$	Normal nonylic or pelargonic acid	$C_8H_{17\alpha}$.COOH	12·5	254
	Isoprimary nonylic or methhexacetic acid .	$C_6H_{13}^{\alpha}.CH(CH_3)$.COOH	liq. at –11	245
$C_{10}H_{20}O_2$	Decylic or capric acid .	C_9H_{19}.COOH	30	269
$C_{12}H_{24}O_2$	Dodecylic or lauric acid	$C_{11}H_{23}$.COOH	43·6	—
$C_{14}H_{28}O_2$	Tetradecylic or myristic acid	$C_{13}H_{27}$.COOH	54	—
$C_{16}H_{32}O_2$	Hexdecylic or palmitic acid	$C_{15}H_{31}$.COOH	62	—
$C_{17}H_{34}O_2$	Heptadecylic or margaric acid	$C_{16}H_{33}$.COOH	59·9	—
$C_{18}H_{36}O_2$	Octadecylic or stearic acid	$C_{17}H_{35}$.COOH	69·2	—
$C_{20}H_{40}O_2$	Arachidic acid . . .	$C_{19}H_{39}$.COOH	75	—
$C_{22}H_{44}O_2$	Behenic acid	$C_{21}H_{43}$.COOH	76	—
$C_{25}H_{50}O_2$	Hyænic acid	$C_{24}H_{49}$.COOH	77	—
$C_{27}H_{54}O_2$	Cerotic acid	$C_{26}H_{53}$.COOH	79	—
$C_{30}H_{60}O_2$	Melissic acid	$C_{29}H_{59}$.COOH	91	—

The acids of this series are commonly termed fatty acids on account of the oily or fatty character of the higher terms. Several of them occur in the free state in nature, as formic acid in ants, in certain caterpillars, and in the nettle; valeric acid in valerian root; and cerotic acid in beeswax. Others are present in the form of ethereal salts in various animal and vegetable products: the essential oils obtained from certain species of *Umbelliferæ* contain substances such as octylic acetate and hexylic butyrate, for example; spermaceti, a crystalline substance found in cavities in the head of the sperm-whale is a cetylic palmitate; and mutton and beef fat chiefly consist of glyceric stearate, and palm oil of glyceric palmitate.

Those containing more than 10 atoms of carbon have all been separated from natural products, and as yet they have not been obtained in isomeric modifications. The lower terms have been prepared by the general methods already described and by various special methods, and of many of them a number of isomerides are already known.

The lowest terms are mobile colourless liquids readily soluble in water, but as the series is ascended the mobility and solubility in water diminishes, and the highest terms are crystalline solids, almost insoluble in water. The liquid members mostly possess more or less characteristic odours.

They furnish crystalline salts, which are less and less soluble in water as the series is ascended. They are bodies of considerable stability, all but the highest terms distilling unchanged. All except formic acid oppose considerable resistance to the action of oxidizing agents; but when sufficiently powerful means are employed, they furnish lower terms of the series, and acids of the succinic series (comp. Herez, *Ann. Chem. Pharm.*, clxxxvi. 257); they yield haloid substitution derivatives without difficulty, but resist the action of concentrated nitric and sulphuric acids.

(1723) FORMIC OR METHYLIC ACID: $CH_2O_2 = H.COOH$.—This acid or its salts occur in ants (*Formica*—hence its name), in the hairs and other parts of the caterpillar of *Bombyx processionea* and other caterpillars, in nettles, and in the perspiration and other secretions of the human body. According to Chapman (*Jour. Chem. Soc.*, xx. 133), a minute amount of formic acid is obtained when pure carbon is oxidized with permanganic acid; it is also formed in small quantity on passing the silent electric discharge through a mixture of carbonic anhydride and hydrogen (Brodie, *Proc. Roy. Soc.*, xxi. 245): $CO_2 + H_2 = CH_2O_2$; and it is a product of the oxidation of methylic alcohol, and of a very large number of carbon compounds, especially highly-oxygenated bodies such as sugar, starch, &c., although the amount obtained in this way is but small on account of the readiness with which it undergoes further oxidation.

Formic acid or formates are obtained in many other ways; for example: by reduction of carbonic acid, as when potassium is exposed in an atmosphere of moist carbonic anhydride (Kolbe and Schmitt): $CO(OH)_2 + H_2 = H.COOH + OH_2$; or when sodium amalgam acts upon a strong aqueous solution of ammonic carbonate (Maly); by heating moist potassic hydrate with carbonic monoxide at 100° (212° F.) for some hours (Berthelot): $CO + HOK = H.COOK$; by heating hydrocyanic acid with water and an acid or an alkali; by the action of potassic hydrate on trichloromethane (chloroform): $HCCl_3 + 4HOK = 3KCl + 2OH_2 + H.COOK$; and by heating the acids of the lactic series of the form $C_nH_{2n+1}.CH(OH).COOH$, with dilute sulphuric acid; for example: $CH_3.CH(OH).COOH + OH_2 = CH_3.CH(OH)_2 + H.COOH$.

It is best prepared by Lorin's method, by heating oxalic acid with glycerol (glycerin).

When oxalic acid is heated alone, it is resolved into carbonic anhydride and formic acid: $COOH.COOH = CO_2 + H.COOH$, but this decomposition only takes place at an elevated temperature, and much of the formic acid is in consequence resolved into carbonic oxide and water; in presence of glycerol, however, the decomposition commences below 50° (122° F.), and is completed below 110° (230° F.), little or no carbonic oxide being produced. Apparently the glycerol promotes the decomposition of the oxalic acid in virtue of the tendency which it has to react with formic acid, producing a basic ethereal salt (glycerol monoformin): $C_3H_5(OH)_3 + H.COOH = H.COO(C_3H_5OH_2 + (OH)_2$; this salt is decomposed by heating with water, yielding glycerol and formic acid: $H.COO.C_3H_5(OH)_2 + OH_2 = H.COOH + C_3H_5(OH)_3$.

Lorin recommends the following mode of proceeding:—1·12 kilograms of glycerol and 3 kilos. of powdered ordinary oxalic acid ($H_2C_2O_4 + 2OH_2$) are placed in a large retort, and the mixture heated over a naked flame; as soon as formic acid begins to distil over, fresh oxalic acid is added in such quantity as to maintain as nearly as possible the original level of liquid in the retort. The acid is added only twice a day, and the retort is cooled a little before each addition of oxalic acid; the same quantity of glycerol suffices to decompose a relatively very large amount of oxalic acid. The distillate is almost of constant strength, and contains about 56 per cent. of formic acid; by distilling it again, a liquid containing about 77·5 per cent. of acid, which boils constantly at 107° (224°·6 F.), may be separated, and by dissolving anhydrous oxalic acid in this with the aid of a gentle heat, allowing to cool, and then distilling the portion which remains liquid, a product is obtained which when well cooled solidifies to a mass of crystals of anhydrous formic acid. By distilling dehydrated oxalic acid with glycerol, a 75 per cent. solution of formic acid may be obtained directly, but on account of the frothing the temperature must be very carefully watched.

Anhydrous formic acid may also be prepared by decomposing carefully dried cupric or plumbic formate—preferably the former—by sulphuretted hydrogen at a temperature not exceeding 100° (212° F.).

The decomposition of oxalic acid may be effected in a similar manner by means of other polyhydric alcohols, such as ethylenic glycol, erythrol, mannitol, dulcitol, and quercitol; the temperature of commencing decomposition is lower when the glycols are employed than with glycerol, but with erythrol and the other alcohols the evolution of gas commences only at about 75° (167° F.); and dulcitol requires a higher temperature than mannitol (Lorin).

Formic acid is a colourless, inflammable, highly corrosive, pungent-smelling liquid, of the sp. gr. 1·22 at 20° (68° F.); it boils at about 100° (212° F.). When cooled to a temperature below 0° (32° F.), it crystallizes in large brilliant plates, melting at 8°·5 (47°·3 F.). It mixes in all proportions with water, alcohol, and ether. On account of the readiness with which it undergoes oxidation to carbonic acid, formic acid is a powerful reducing agent: thus, when it is heated with a solution of mercuric chloride, mercurous chloride is precipitated; a cold aqueous solution dissolves mercuric oxide, but when the liquid is gently heated, white micaceous crystals of mercurous formate at once separate, and carbonic anhydride is evolved; whilst, if the solution be boiled, nothing but metallic mercury is precipitated; similarly, argentic oxide is instantly reduced by the heated acid, but is dissolved by the cold acid. Formic acid is resolved into carbonic oxide and water by heating gently with concentrated sulphuric acid; chlorine converts it into hydrochloric acid and carbonic anhydride.

It forms with water an unstable 'hydrate,' *orthoformic acid*,[*] $HC(OH)_3$, which boils constantly at 107° (224°·6 F.) under a pressure of 760 mm. of mercury (Roscoe, *Jour. Chem. Soc.*, xv. 271); when distilled under a lower pressure this hydrate loses acid, and when distilled under a higher pressure it loses water, the boiling point falling or rising accordingly, but all mixtures of formic acid and water ultimately attain approximately the composition $HC(OH)_3$ when distilled under the ordinary atmospheric pressure.

Formates.—These are mostly easily soluble in water. The most characteristic are *cupric formate*, $(HCO_2)_2Cu + 4OH_2$, which forms large bright blue monoclinic prisms; and *plumbic formate*, $(HCO_2)_2Pb$, which crystallizes in colourless shining rhombic prisms. Argentic formate is white, but quickly turns black even in the dark, and is immediately decomposed when heated. Basic plumbic formates such as $HCO_2.Pb.O.Pb.CO_2H$ are produced on boiling solutions of the normal salt with plumbic oxide. By dissolving potassic and sodic formates in aqueous formic acid and evaporating in vacuo, crystals of acid salts are obtained which may be regarded as derived from "orthoformic acid," thus: $HCO_2Na + HCO_2H + OH_2 = HC(ONa)(OH).O.CH(OH)_2$; and mixed salts containing copper or zinc and barium, which may also be regarded as derivatives of this acid, are formed on evaporation of mixed solutions of the simple salts. Solutions of formates are coloured blood-red by the addition of ferric chloride. On evaporating in vacuo a solution of ferrous formate oxidized by nitric acid, the basic ferric formonitrate $Fe_2(HCO_2)_2(NO_3)_2(OH)_2$ is deposited in red iridescent crystals; a solution of ferrous chloride in formic acid similarly treated yields the compound $Fe_2Cl_2(HCO_2)_4$; and by oxidizing a mixture of equivalent quantities of ferrous formate and acetate with nitric acid, the formacetonitrate $Fe_2(HCO_2)_2(CH_3.CO_2)_2(OH)_2$ is produced.

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[*] Properly speaking this compound is not an acid, but a trihydric alcohol (*acidhydrol*), homologous with glycerol (glycerin), bearing the same relation to the parent acid that the aldehydrols bear to the aldehydes (comp. 1491). So-called *ethylic orthoformate*, $HC(OC_2H_5)_3$, the mixed ether derived from it and ethylic alcohol, and which is obtained by the action of sodic ethylate on trichloromethane, is a perfectly stable compound; it is a colourless liquid, of pleasant aromatic odour, almost insoluble in water, boiling at 146° (294°·8 F.).

(1724) **ACETIC OR ETHYLIC ACID**: $C_2H_4O_2 = CH_3.COOH$.—Acetic acid or its salts occur in small quantity in the juices of many plants and in several animal secretions. It may be formed by the methods already described from methane, ethaldehyde, and ethylic alcohol. On exposing sodic methide to the action of carbonic anhydride, these two compounds combine, forming sodic acetate (Wanklyn): $CH_3Na + CO_2 = CH_3.CO_2Na$; according to Berthelot, if a mixture of equal volumes of acetylene and oxygen is exposed over potassic hydrate solution, it is gradually absorbed with formation of potassic acetate, and the acid itself is formed by oxidation of acetylene with a solution of pure chromic acid. On the large scale, acetic acid is prepared either by the distillation of wood, or by the atmospheric oxidation of a dilute aqueous solution of alcohol.

In preparing it by the former method, the acid liquid which distils over (1285) is again distilled, and the portion which first passes over, consisting chiefly of methylic alcohol and acetone, is collected apart; the crude acid which is afterwards collected is neutralized with milk of lime, and the resulting impure solution of calcic acetate is mixed with a solution of sodic sulphate: the solution of sodic acetate thus formed is drawn off from the calcic sulphate, and evaporated to the crystallization point, and the crystals of sodic acetate are then dried and carefully fused in order to expel and decompose adherent tarry matter; finally the fused salt is recrystallized from water, and decomposed by distillation with hydrochloric or sulphuric acid. To obtain the anhydrous acid, dehydrated sodic acetate is decomposed by the equivalent quantity of concentrated sulphuric acid (comp. 1690).

In Germany and other countries where alcohol is cheap, dilute acetic acid is prepared by oxidation of alcohol, which is effected by allowing the diluted spirit to trickle slowly over a large surface of wood shavings or birch twigs contained in vats of suitable construction provided with a row of apertures near the bottom to admit air. In this country vinegar (*acetum*) is prepared in a similar manner from a weak malt-wort which has been allowed to ferment in contact with beer yeast. The formation of acetic acid in this manner is not the result of the immediate oxidation of the alcohol by the atmospheric oxygen, nor is it to be attributed to the great extent of surface over which the alcohol is spread, but it is in some way induced by a microscopic organism, the *Mycoderma aceti*. If this organism be rigidly excluded, no acetic acid whatever is formed, however great the surface over which the dilute alcohol is spread (Pasteur; A. Mayer). The mycoderm apparently exercises an influence similar to that of finely-divided platinum, and quite different from that of yeast and other microscopic organisms which excite fermentation.

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Pure acetic acid forms large colourless transparent crystals, melting at 16°·7 (62° F.); in the liquid state it is a colourless, mobile, pungent-smelling substance, boiling at 118° (244°·4 F.). It is highly corrosive, and raises blisters on the skin. It is miscible in all proportions with water, alcohol and ether, and is itself a good solvent for many substances. According to Mendeleff, acetic acid has the sp. gr. 1·0607 at 15° (59° F.) referred to water at 4° (39°·2 F.). On diluting the acid with water, the sp. gr. increases up to a certain point, but according to Roscoe and Oudemanns the maximum density of mixtures of acetic acid and water bears no relation to a fixed equivalent proportion of the acid and water, but corresponds to a different proportion for each particular temperature. The mixtures which exhibit the maximum density, however, are not far removed in composition from a hydrate of the formula $C_2H_4O_2 + OH_2 = CH_3.C(OH)_3$, and there can be little doubt that an aqueous solution of acetic acid at least partially consists of this 'acidhydrol;' it is, however, a much less stable compound than the homologous 'methacidhydrol' derived from formic acid, mixtures of acetic acid and water, whatever the proportions of the constituents, being decomposed by distillation in such a manner as ultimately to leave a residue of the almost anhydrous acid, no mixture exhibiting a constant boiling point or distilling of approximately constant composition (Roscoe). The mixed ether derived from 'ethacidhydrol' and ethylic alcohol, $CH_3.C(OC_2H_5)_3$, obtained by heating β-trichlorethane, $CH_3.CCl_3$, with sodic ethylate and ether in sealed tubes at 100°—120° (212°—248° F.), is a colourless liquid, boiling constantly at 142° (287°·6 F.) (Geuther, *Jahresb.*, 1870, 636).

At temperatures near to its boiling point, under the ordinary pressure, the vapour of acetic acid has a density considerably greater than corresponds to the formula $C_2H_4O_2$, and only exhibits the normal density at about 250° (482° F.), but under a pressure of about 20 mm. the vapour has nearly its normal density even at ordinary temperatures. Hence it appears that the molecules of acetic acid vapour are not similarly constituted at all temperatures and under all pressures, but that a given quantity of acetic acid forms a smaller number of molecules at low than at high temperatures, and a greater number of molecules at low than at high pressures (comp. Horstmann, *Deut. chem. Ges. Ber.*, iii. 78; Naumann, *ibid.*, iii. 702). It is not improbable that the increased density is due to the presence of molecules of the formula $C_4H_8O_4$, the relation of which to the simpler molecules $C_2H_4O_2$ may be expressed by the formulæ:

$$CH_3.COOH \qquad\qquad CH_3.C(OH)\left\{\begin{matrix}O\\O\end{matrix}\right\}C(OH).CH_3;$$

or it perhaps results merely from the mean distances between the molecules being less.

Acetic acid is a very stable substance, being scarcely affected by ordinary oxidizing agents or concentrated nitric acid, or by fusion with alkalies. On passing its vapour through red-hot tubes the greater part remains unaltered, but a portion is decomposed, dimethylketone and methane being the principal products. By the action of chlorine in sunshine, it is converted into chlorinated derivatives, brominated derivatives being formed by heating it with bromine.

Acetates.—Acetic acid forms a large number of metallic salts, which mostly crystallize well and dissolve readily in water. In addition to the *normal potassic salt*, $KC_2H_3O_2$, which is extremely soluble in water and crystallizes with difficulty, it forms a *hyperacid salt*: $KC_2H_3O_2.C_2H_4O_2 = (?)\ CH_3.C(OK)\left\{\begin{matrix}O\\O\end{matrix}\right\}C(OH).CH_3$, which may be obtained by dissolving the normal salt in an excess of acid and evaporating the solution; it crystallizes in long, flattened prisms, melting at 148° (298°·4 F.), and when heated to about 200° (392° F.) it is resolved into the normal salt and acetic acid. The corresponding sodic salt is similarly decomposed, and this property affords a convenient means of obtaining anhydrous acetic acid. By dissolving potassic acetate in boiling acetic anhydride, the compound $2KC_2H_3O_2.C_4H_6O_3$ is said to be produced; it crystallizes in colourless needles.

Sodic acetate, $NaC_2H_3O_2 + 3OH_2$, crystallizes readily in large efflorescent rhombic prisms, soluble in about 3 pts. of cold water; the anhydrous salt melts at 288° (550°·4 F.), and begins to decompose at about 315° (599° F.). Two hyperacid sodic salts may be obtained, $NaC_2H_3O_2.C_2H_4O_2$ and $NaC_2H_3O_2.2C_2H_4O_2$ (comp. Lescœur, *Compt. Rend.*, lxxxiv. 1029); and by dissolving the normal salt in boiling acetic anhydride, Perkin (*Jour. Chem. Soc.*, xxi. 185) has obtained the compound $NaC_2H_3O_2.C_4H_6O_3$.

Ammonic acetate, $NH_4C_2H_3O_2$, is formed on saturating dry acetic acid with ammonia gas, but the tendency to form the hyperacid salt is so great, that on evaporating the aqueous solution of the normal salt, ammonia is given off, and the latter remains. On distillation, ammonic acetate is resolved into water and acetamide: $CH_3.COONH_4 = CH_3.CO.NH_2 + OH_2$.

Baric, calcic and *strontic acetates* are very soluble, but crystallize readily; *magnesic acetate* crystallizes with difficulty.

Argentic acetate, $AgC_2H_3O_2$, crystallizes from hot water in thin, flat, glistening, flexible needles; it dissolves in about 100 pts. of cold water, but is somewhat more soluble in hot water.

Plumbic acetate (sugar of lead), $Pb(C_2H_3O_2)_2 + 3OH_2$, crystallizes in efflorescent monoclinic prisms, soluble in about $1\frac{1}{2}$ pts. of cold water, and in about 8 pts. of alcohol; the aqueous solution has an intensely sweet astringent taste: it does not yield a precipitate with ammonia in the cold, but is partially decomposed by carbonic acid. By digesting the solution of the normal acetate with plumbic oxide, two *basic plumbic acetates* are formed: the first $[CH_3.COO(PbOH)]_2 + OH_2$ or $CH_3.COO.Pb.O.Pb.O.COO.CH_3 + 2OH_2$ is prepared by dissolving the requisite amount of oxide in the solution of the acetate; the second, $(CH_3.COO.PbO)_2Pb$ by boiling a solution of 6 pts. of the normal salt with 7 pts. of the oxide, or by allowing a saturated solution of the normal salt mixed with one-fifth its volume of ammonia to evaporate: it forms long silky needles, very soluble in water, but insoluble in alcohol. A less basic salt is said to be formed by heating the normal salt until it melts and subsequently solidifies in a white porous mass, more basic salts by boiling the normal salt with an excess of the oxide (comp. Loew, *Jour. pr. Chem.*, xcviii. 385). The basic salts are all decomposed by carbonic anhydride, and converted into the normal salt and basic carbonate (white lead); they furnish precipitates with a large number of hydroxyl compounds which are not precipitated by the normal acetate.

Cupric acetate, $Cu(C_2H_3O_2)_2$, below 8° (46°·4 F.), crystallizes with 5 mols. of water in large blue prisms, but above this temperature it forms beautiful dark-green crystals containing only a single mol. of water; its aqueous solution is decomposed by boiling with separation of a difficultly soluble basic salt $(Cu(C_2H_3O_2)_2.CuO)$, of which several are known corresponding in composition to the basic plumbic acetates. Common verdigris, obtained by exposing plates of copper to the air in contact with acetic acid, is a mixture of basic cupric acetates, the blue variety consisting chiefly of that of the formula $(C_2H_3O_2)_2Cu.CuO)$, and the green of that of the formula $2(C_2H_3O_2)_2Cu.CuO$.

Neutral solutions of acetates are coloured red by ferric chloride in consequence of the formation of ferric acetate; this salt is uncrystallizable and extremely soluble. On boiling its solution, a basic salt is precipitated, the liquid becoming colourless. The basic ferric salts have been examined by Scheurer-Kestner (see Watts' *Dict.*, 1*st Sup.*), who has also prepared an interesting series of mixed acetonitrates such as the tetracetodinitrate, $Fe(C_2H_3O_2)_4(NO_3)_2$, by dissolving ferric hydrate in mixtures of acetic and nitric acid in various proportions.

Aluminic acetate is of importance on account of its employment in calico printing, for which purpose it is prepared by precipitating a solution of alum with one of plumbic acetate; the liquid is thickened by gum or other suitable material, and with it the design is impressed upon the cloth. On exposure to a moderate degree of heat, the acetate is decomposed, acetic acid being given off and alumina remaining in a state capable of entering into combination with the colouring matter. According to Crum (*Jour. Chem. Soc.*, vi. 216), the normal acetate cannot be isolated from such a solution, and its existence therein is even doubtful; but if, for example, the liquid be evaporated at a low temperature with sufficient rapidity, by spreading it in a thin layer over sheets of glass heated to not more than 37°·5 (99°·5 F.), a substance is obtained which is readily dissolved by water consisting apparently of the hydrated basic salt $Al(OH)_2(C_2H_3O_2)_4$. If, however, a solution containing about 5 per cent. of alumina is set aside at a temperature of 15°—21° (59°—69°·8 F.), it begins after four or five days to deposit a crust, and if the solution be heated it deposits a heavy white powder; these substances are apparently basic tetracetates like the preceding, but having different amounts of water associated with them, and they are insoluble in water. By the continued action of heat on a weak solution of the soluble tetracetate, this salt is almost entirely decomposed; but the alumina remains in solution, and as thus prepared, it no longer possesses the power of acting as a mordant. Graham has shown that if such a solution be dialysed, almost the whole of the acid is removed, and a solution is obtained which is coagulated by minute quantities of acids, of alkalies and of most salts; the precipitate, moreover, is insoluble in acids.

(1725) PROPIONIC or PROPYLIC ACID; *methacetic acid:* $C_3H_6O_2 = CH_3.CH_2.COOH$.—Originally this acid was termed *metacetonic* acid, having been first obtained by Gottlieb in 1844 by oxidation of metacetone (p. 788); it may be formed by the general methods already described from ethane, ethylic alcohol, propylic alcohol and propaldehyde, and in many other ways besides; for example, as sodic salt by the direct combination of carbonic anhydride and sodic ethide: $CO_2 + NaC_2H_5 = C_2H_5.COONa$ (Wanklyn); in minute quantity as potassic salt by the combination of carbonic monoxide with potassic ethylate: $CO + C_2H_5.OK = C_2H_5\,COOK$ (Hagemann, *Deut. chem. Ges. Ber.*, iv. 877); by heating ordinary lactic acid, $CH_3.CH(OH).COOH$, with a concentrated solution of hydriodic acid; by heating isosuccinic acid to fusion: $CH_3.CH(COOH)_2 = CH_3.CH.COOH + CO_2$; and as ethylic salt by heating ethylic acetomethacetate, $CH_3.CO.CH(CH_3).COOC_2H_5$, with sodic ethylate.

It is usually prepared by oxidation of propylic alcohol, or from cyanethane (comp. Linnemann, *Ann. Chem. Pharm.*, cxlviii. 251; Philippi and Tollens, *ibid.*, clxxi. 315; Beckurt and Otto, *Deut. chem. Ges. Ber.*, x. 262); according to Freund (*Jour. pr. Chem.* [2], v. 446), it may conveniently be prepared by the reduction of lactic acid with hydriodic acid.

Propionic acid closely resembles acetic acid in its properties; it boils at 140°·7 (285°·3 F.), and at 19° (66°·2 F.) has the sp. gr. ·9961 (Linnemann). It does not solidify when cooled to −21° (−5° 8 F.). It is miscible with water in all proportions, and is not separated from the solution by salts; the anhydrous acid absorbs water on exposure to moist air.

Propionates.—The *baric* and *calcic* salts are both soluble in less than 2 pts. of water at 17° (62°·6 F.). *Argentic propionate*, $C_2H_5.COOAg$, crystallizes from water, according to the concentration of the solution, either in plates or needles, the latter being occasionally grouped in bundles which are often extremely small; 1 pt. dissolves in 119 pts. of water at 18° (64°·4 F.). *Plumbic propionate* is easily soluble and amorphous. If its solution is evaporated to dryness with an excess of plumbic oxide, a basic salt, $3(C_2H_5.CO_2)_2.Pb + 2PbO$, is produced which may be extracted with cold water, and on boiling and well stirring the filtered liquid, it is again suddenly deposited; by means of this salt propionic acid may readily be distinguished and separated from formic and acetic acids, which yield basic salts insoluble in cold water, whereas the salt in question requires only 8—10 pts. of water at 14° (57°·2 F.) to dissolve it (Linnemann, *Ann. Chem. Pharm.*, clx. 218).

(1726) TETRYLIC OR BUTYRIC ACIDS: $C_4H_8O_2$.—Both the possible acids of the formula $C_3H_7.COOH$ are known—viz., *normal (primary) butyric* or *ethacetic acid*, $CH_3.CH_2.CH_2.COOH$, and *iso-* or *secondary butyric* or *aimethacetic acid*, $CH(CH_3)_2.COOH$.

Normal butyric acid may be formed from normal tetrane, normal primary butylic alcohol and tetraldehyde, normal propylic alcohol, and ethylic acetoethacetate by the general methods; it is produced in small quantity, together with its lower homologues, by oxidation of albuminous substances, and from many other substances by oxidation or by the action of fused potassic hydrate (comp. Grünzweig, *ibid.*, clxii. 193). It is produced in considerable quantity, together with acetic and caproic acids, by fermentation of lactic acid, and is most readily prepared in this way; tartaric acid and a number of other substances also furnish this acid on fermentation. It occurs in small quantity as glyceric salt in butter, whence the name butyric acid; in various animal secretions, probably in the form of sodic salt; and in the free state in perspiration, and the secretions of many insects. The oils from the fruit of various species of *Umbelliferæ* also contain ethereal salts of butyric acid: ethylic butyrate being a constituent of the oils of *Heracleum giganteum* and *H. spondylium*, hexylic butyrate being also present in the latter; the oil from the seeds of the common parsnep (*Pastinaca sativa*) consists chiefly of octylic butyrate (comp. Möslinger, *ibid.*, clxxxv. 26).

In the pure state butyric acid is a colourless liquid, having an odour similar to that of acetic acid, and only exhibits a rancid odour when volatilized or diluted; it boils at 162°·4 (324°·3 F.), and at 14° (57°·2 F.) has the sp. gr. ·958; when cooled it solidifies to a mass of crystals, which melt at about 0° (32° F.) (Linnemann). It dissolves in water in all proportions, but may be separated by the addition of soluble salts; the acid thus separated, however, retains a considerable quantity of water, and probably, at least in part, consists of the hydrate $C_3H_7.COOH + OH_2 = C_3H_7.C(OH)_3$. It is oxidized with very considerable difficulty, but by heating it for some time with an excess of chromic acid mixture it is completely converted into water, acetic acid and carbonic anhydride (Grünzweig); by long-continued boiling with nitric acid (sp. gr. 1·4) it is oxidized to succinic acid, $COOH.CH_2.CH_2.COOH$ (Erlenmeyer, Sigel and Belli, *ibid.*, clxxx. 207).

Butyrates.—Calcic butyrate, $(C_3H_7.CO_2)_2Ca + OH_2$, crystallizes on spontaneous evaporation of its aqueous solution in rhombic plates or broad glistening needles grouped in bundles; it dissolves in about 3½ pts. of cold water, but is much less soluble in hot water, a cold *saturated* solution becoming almost solid from separation of the salt when heated in the water bath. Erlenmeyer has observed that when a tube containing a cold saturated solution of this salt was heated perhaps 30 or 40 times at intervals during a period of about 10 years, the calcic salt of isobutyric acid was produced, about $\frac{1}{10}$ to $\frac{1}{12}$ of the normal salt undergoing this change; as this was not observed to take place when a solution was boiled for 8 days, it appears probable that time is of influence (*ibid.*, clxxi. 126).

Argenticbutyrate, $C_3H_7.COOAg$, mostly crystallizes from a hot saturated solution in bundles or cauliflower-like groups of glistening plates, soluble in about 72 pts. of boiling water and in about 200 pts. of water at 14° (57°·2 F.); the character of the crystals is much influenced by the presence of small quantities of the salts of homologous acids, traces of acetate causing them to assume moss-like forms. *Zincic butyrate*, $(C_3H_7.CO_2)_2Zn + 2OH_2$, forms flat monoclinic prisms, which effloresce on exposure to the air; it dissolves in about 10 pts of cold water; on evaporating its aqueous solution a basic salt separates. Many of the butyrates and acetates crystallize together, forming double salts.

Isobutyric acid occurs together with formic, acetic, propionic and benzoic acids in the banana, the fruit of *Ceratonia siliqua* (Grünzweig); it may be produced by oxidation of isobutylic alcohol and isobutyric aldehyde, from isopropylic alcohol, by converting it into the cyanide, &c., and by heating ethylic acetodimethacetate, $CH_3.CO.C(CH_3)_2.COOC_2H_5$, with sodic ethylate. It exactly resembles the normal acid in odour, but boils at 154° (309°·2 F.), and at 20° (68° F.) has the sp. gr. ·9503; it is soluble in five times its weight of water at 20° (68° F.). Isobutyric acid is much more readily oxidized by chromic acid mixture than butyric acid, but furnishes the same products (Grünzweig).

Isobutyrates.—Calcic isobutyrate, $(C_3H_7.CO_2)_2Ca + 5OH_2$, crystallizes in monoclinic prisms, and is distinguished from the isomeric salt by being much more soluble in hot than in cold water. *Argentic isobutyrate*, $C_3H_7.COOAg$, forms transparent plates, and requires only 110 pts. of water at 16° (60°·8 F.) for its solution. *Zincic isobutyrate*, $(C_3H_7.CO_2)_2Zn + OH_2$, is rapidly decomposed by boiling its aqueous solution with separation of a basic salt.

(1727) PENTYLIC OR VALERIC ACIDS: $C_5H_{10}O_2$.—The four possible isomeric pentylic acids have all been obtained. *Normal primary valeric acid*, or *propacetic acid:* $CH_3.CH_2.CH_2.CH_2.COOH$, was first obtained by Lieben and Rossi (*ibid.*, clix. 58) from butylic cyanide from normal butylic alcohol; it has also been obtained by oxidation of normal primary amylic alcohol from normal pentane and of methylamylketone (Schorlemmer), and by oxidation of *a*-oxycaproic acid (Erlenmeyer, *Deut. chem. Ges. Ber.*, ix. 1839). In odour it more closely resembles butyric acid than ordinary valeric acid; it boils at 184°—185° (363°·2—365° F.) under a pressure of 736 mm. of mercury, and at 0° (32° F.) has the sp. gr. ·957. It does not solidify when cooled to −16°

(3°·2 F.). It requires about twenty-seven times its volume of water for its solution, and itself dissolves about 1-10th its volume of water, but may be dehydrated by distillation.

Valerates.—Calcic valerate, $(C_4H_9.CO_2)_2Ca + OH_2$, forms glistening scales, and like calcic butyrate is more soluble in cold than in hot water, the point of least solubility being about 70° (158° F.); although the crystals which separate on cooling a boiling saturated solution, or heating a cold saturated solution, to this temperature are in great part redissolved as the solution is further cooled or heated, there is always a certain residue, and it would appear probable therefore that a basic salt is produced. *Baric valerate* crystallizes in small anhydrous plates, soluble in six times their weight of water at 10° (50° F.), and more soluble in hot water.

Isoprimary valeric or *isopropacetic acid; ordinary valeric* or *valerianic acid:* $CH(CH_3)_2.CH_2.COOH$.—This acid occurs in valerian and angelica root, and in the berries and bark of the guelder rose (*Viburnum opulis*); it is a product of the decay of albuminous substances. It may be formed by oxidation of the optically inactive isoprimary amylic alcohol contained in fusel oil, and from isobutylic alcohol by conversion into isobutylic cyanide, &c. (Erlenmeyer and Hell, *Ann. Chem. Pharm.*, clx. 257), also from ethylic acetoisopropacetate, $CH_3.CO.CH(C_3H_7)^{\beta}.COOH$; and on oxidation of leucin or amidocaproic acid (q. v.). Isopropacetic acid is a thin oily liquid, of peculiar unpleasant odour like that of decayed cheese; it boils at about 175° (347° F.), and at 0° (32° F.) has the sp. gr. ·947. It is slightly more soluble in water than propacetic acid, which cannot be completely dehydrated by distillation; when boiled with chromic acid mixture, it is oxidized to acetic acid, carbonic anhydride and water.

Isovalerates.—Argentic isopropacetate, $C_4H_9.COOAg$, crystallizes from solutions containing free acid, especially acetic acid, in large glistening plates, which dissolve in 540 pts. of water at 20° (68° F.) The *baric salt*, $(C_4H_9CO_2)_2Ba$, crystallizes readily either in thin narrow triclinic prisms or larger broader plates; it dissolves in about its own weight of water at 22° (71°·6 F.).

Secondary valeric or *methethacetic acid; optically active valeric acid:* $CH_3.CH(C_2H_5).COOH$.—This modification is formed by oxidation of the optically active amylic alcohol contained in fusel oil (comp. 1438); according to Erlenmeyer and Hell, it is also present in the acid from valerian root, and is produced together with the isoprimary acid by oxidation of amidocaproic acid or leucin. It has been obtained in a pure state by Saur from ethylic acetomethethacetate, $CH_3.CO.C(CH_3)(C_2H_5).COOC_2H_5$, by distillation with sodic ethylate and saponification of the resulting ethylic salt (*Ann. Chem. Pharm.*, clxxxviii. 257). The acid thus prepared is a thin liquid of less unpleasant odour than ordinary valeric acid, boiling at 173° (343°·4 F.); it does not mix in all proportions with water, but is dehydrated with difficulty. The acid formed by synthesis appears to differ from that obtained in other ways, by being optically inactive, but this is the only distinction. It has not been ascertained whether the synthetic acid is optically active; the most active specimen as yet prepared by oxidation of amylic alcohol had the rotatory power $(\alpha)_D = +61^\circ \cdot 2$ (Ley). According to Erlenmeyer and Hill, the active acid becomes inactive on heating with a small quantity of sulphuric acid at 250° (482° F.), but is otherwise unaltered in its properties.

Methethacetates.—Argentic methethacetate crystallizes from hot water in needles grouped in feather-like forms, almost insoluble in cold water, but its most characteristic salt is that of barium, which cannot be crystallized, but remains as a gummy mass on evaporation of its solutions.

Tertiary valeric or *trimethacetic acid:* $C(CH_3)_3.COOH$.—This acid was first prepared by Butlerow by displacing the OH group in trimethylcarbinol, $C(CH_3)_3.OH$, by COOH (*ibid.*, clxv. 322; clxx. 151; clxxiv. 355); it has also been obtained by oxidation of methyl tertiary-butyl ketone or pinacolin (1676), and of the homologous ethyl tertiary-butyl ketone (Wischnegradsky, *ibid.*, clxxviii. 103), and by oxidation of the tertiary octylcarbinol, $C(CH_3)_3.CH_2.C(CH_3)_2.OH$ (Butlerow, *ibid.*, clxxxix. 44.)

To prepare it, a mixture of 100 pts. of the iodotrimethylmethane, $CI(CH_3)_3$, obtained by the action of hydriodic acid on trimethylcarbinol, or by combining β-dimethylethylene (isobutylene) with hydriodic acid, 110 pts. of mercuric potassic cyanide, $HgK_2(CN)_4$, and 75 pts. of dry talc powder, is placed in a vessel surrounded by water the temperature of which is not allowed to rise above 5° (41° F.); by this means, the formation of isobutylene is almost entirely avoided, but a considerable quantity of a resinous substance is always produced. After two or three days, when the action is complete, water is added and the product distilled off from the oil bath, and the oily distillate is mixed with about an equal volume of fuming hydrochloric acid, and heated in closed tubes for several hours at 100° (212° F.); the contents of the tubes is then mixed with water, and the oil separated from the aqueous solution, the small amount of acid remaining in solution being recovered by distilling the liquid and saturating the distillate with sodic sulphate. The crude acid is treated with a solution of sodic hydrate, the solution separated from undissolved oil, evaporated to dryness, the residue dissolved in a small quantity of water, and decomposed with sulphuric acid diluted with twice its weight of water; the acid thus obtained is further purified by conversion into the magnesic or zincic salt, and finally is dehydrated by means of phosphoric anhydride. This process, however, furnishes only about one-fourth the theoretical amount.

Trimethacetic acid is solid at ordinary temperatures: the crystallized acid forms angular lamellæ consisting of small needles ranged at right angles from a common axis; it is semi-transparent, but when cooled below 0° (32° F.) it becomes opaque, being converted into a mass of silky needles radiating from a common centre. Both forms belong to the regular system. It melts at 35°·4 (95°·7 F.), and boils at 163°·8 (326°·9 F.). The fused acid is a colourless oil, of the sp. gr. ·905 at 50° (122 F.), soluble in about 40 times its weight of water.

Trimethacetates.—Trimethacetic acid furnishes a number of highly characteristic salts, most of which, although soluble in water, are with difficulty wetted by it; most of them readily lose acid when boiled with water. On adding a concentrated solution of potassic hydrate or carbonate to the acid, the mixture becomes solid at a certain point, but the crystals dissolve on warming, and as the solution cools, fine long needles, grouped in stars, separate out, consisting of the *acid potassic salt*, $C_5H_9KO_2 + 2C_5H_{10}O_2$—($?C_4H_9.C(OK)(C_4H_9.COO)_2$). *Baric trimethacetate* $(C_4H_9.CO_2)_2Ba + 5OH_2$, and *calcic trimethacetate*, $(C_4H_9.CO_2)_2Ca + 5OH_2$, crystallize in needles or prisms; the former is very soluble in water; the latter moderately so. *Magnesic trimethacetate*, $(C_4H_9.CO_2)_2Mg + 8OH_2$, forms large thin transparent plates. *Zincic trimethacetate*, $(C_4H_9.CO_2)_2Zn + OH_2$, crystallizes in large glistening scales, difficultly soluble in water; on warming a cold saturated solution, it gelatinizes, owing to the separation of a basic salt, $C_4H_9.CO_2(Zn.OH)$, which redissolves entirely as the solution cools, if none of the acid has been allowed to escape. *Argentic trimethacetate*, $C_4H_9.COOAg$, is obtained as a very voluminous precipitate on the addition of argentic nitrate to moderately concentrated solutions of other trimethacetates; it is difficultly soluble in water, more soluble in alcohol, and separates from the former in crystals resembling those of argentic acetate, when the solution is allowed to evaporate spontaneously. A number of other trimethacetates have been described by Butlerow.

(1728) HEXYLIC OR CAPROIC ACIDS: $C_6H_{12}O_2$.—Of the eight possible forms of this acid five are at present known.

Normal (primary) Hexylic or *Caproic Acid; Normal Tetrylacetic Acid:* $CH_3.CH_2.CH_2.CH_2.CH_2.COOH$, has been obtained from normal primary amylic alcohol by displacing the OH group by COOH in the usual manner (Lieben and Rossi), and by oxidation of normal primary hexylic alcohol (Franchimont and Zincke); it occurs in small quantity as octylic salt in the oils of *Heracleum sphondylium* and *Pastinaca sativa.* The caproic acid present in the free state in perspiration, as glyceric salt in butter, cocoa-nut oil (in considerable amount), and other fatty substances, and which is obtained by oxidation of albuminous bodies and fats, is probably the normal acid. It is formed together with acetic and butyric acids by fermentation of lactic acid, and is most readily prepared in this manner, being separated from these acids by fractional distillation and washing with water, in which it is only slightly soluble.

Normal caproic acid is a colourless mobile oil, of pungent, unpleasant odour, boiling at about 205° (401° F.); of the sp. gr. ·945 at ·0° (32° F.); when strongly cooled it solidifies to a white crystalline mass, melting at about −2° (28°·4 F.) It forms a crystalline compound with calcic chloride, a property which it apparently shares with its lower homologues (Lieben and Janeck). By oxidation with nitric acid it is resolved into succinic and acetic acids (Erlenmeyer, Sigel and Belli):

$$CH_3.CH_2.CH_2.CH_2.CH_2.COOH + 5(O + OH_2) = CH_3COOH + COOH.CH_2.CH_2.COOH + 6OH_2.$$

Caproates.—*Calcic caproate*, $(C_5H_{11}CO_2)_2Ca + OH_2$, forms long very thin glistening prismatic plates; 100 pts. of a solution saturated at 18°·5 (65·3 F.) contain 2·7 pts. of the anhydrous salt, and it is only slightly more soluble in hot water. *Baric caproate* forms indistinct crystals, which apparently are sometimes anhydrous, and sometimes contain water of crystallization; its solubility is variously stated at 8—12 pts. of anhydrous salt in 100 pts. of the solution saturated at about 20° (68° F.) (comp. Lieben and Janeck, *ibid.*, clxxxvii. 126; Erlenmeyer, *ibid.*, clxxx. 215).

Isoprimary Hexylic or *Caproic Acid; Isoprimary Tetrylacetic Acid:* $(CH_3)_2CH.CH_2.CH_2.COOH$, has been obtained by saponification of ethylic acetoisotetrylacetate (Rohn, *ibid.*, cxc. 316); by displacing the OH group in the inactive amylic alcohol of fusel oil by COOH (Lieben and Rossi), and as sodic salt by the combination of carbonic anhydride with the compound NaC_5H_{11} prepared from this alcohol (Wanklyn and Schenck), but the acid thus obtained is impure; and by heating pyroterebic acid with hydriodic acid (Mielck, *ibid.*, clxxx. 57). It is a colourless oil of unpleasant odour; boiling at about 199° (390°·2 F.), of the sp. gr. ·931 at 0° (32° F.); it does not solidify when cooled to − 18° (0·4° F.).

Isocaproates.—According to Rohn, the *calcic* and *baric salt* both crystallize in *anhydrous* needles grouped in bundles, whereas Lieben and Rossi and Mielck state that the calcic salt contains 3 mols. of water, and the baric salt one or two; the statements as to the solubility of these salts are also very discrepant.

Secondary Hexylic Acid.—Diethacetic acid: $(C_2H_5)_2CH.COOH$, obtained by saponification of ethylic acetodiethacetate, $CH_3.CO.C(C_2H_5)_2.COOC_2H_5$, or by dry distillation of the diethoxybutyric acid, $CH_3.CH(OH).C(C_2H_5)_2.COOH$, is an oil of peculiar odour quite different from that of the normal acid. The silver salt crystallizes in silky asbestos-like needles united in forms resembling fern fronds: it is as soluble as argentic acetate, and rapidly blackens on exposure to light, whereas the salt of the normal acid is scarcely affected by light. The baric salt also crystallizes well (Frankland and Duppa; Schnapp, *Deut. chem. Ges. Ber.*, x., 1953).

Tertiary Hexylic Acid.—Dimethethacetic Acid: $(CH_3)_2C(C_2H_5).COOH$, is prepared from dimethylethylcarbinol in precisely the same way that tertiary valeric acid is from trimethylcarbinol. The isocaproic acid obtained by Markownikoff (*Zeits. Chem.* [2], ii. 502) from amylene was probably this acid in an impure state. Dimethacetic acid is a colourless liquid insoluble in water, having a slight odour like that of the other acids of the series, boiling at 187° (368° 6 F.); it solidifies at low temperatures, and melts at − 14°(6°·8 F.). The *baric salt*, $(C_5H_{11}.CO_2)_2Ba + 5OH_2$, crystallizes in large transparent plates, easily soluble in water. The *zincic salt*, $(C_5H_{11}.CO_2)_2Zn$, crystallizes in transparent prisms, and behaves like that of trimethacetic acid on heating its cold saturated solution. The *silver salt* crystallizes from a hot saturated solution in fine silky needles, quite different from the trimethacetate. The magnesic salt is extremely soluble and does not crystallize (Wischnegradsky, *Ann. Chem. Pharm.*, clxxiv. 56).

(1729) HEPTYLIC OR ŒNANTHYLIC ACID: $C_7H_{14}O_2$.—Only one of the large number (17) of possible heptylic acids has been investigated.

Normal (primary) Heptylic or *Œnanthylic Acid:* $CH_3.(CH_2)_5.COOH$, is obtained by oxidation of normal heptylic alcohol and of normal heptylic aldehyde (œnanthol), and by displacing the OH group in normal hexylic alcohol by COOH; it is also formed on oxidation of castor oil and oleic acid; it is most readily prepared by oxidation of œnanthaldehyde (comp. Grimshaw and Schorlemmer, *Jour. Chem. Soc.*, xxvi. 1073). It is a limpid oily liquid, boiling at 223°—224° (433°·4—435°·2 F.), of the sp. gr. ·9345 at 0° (32° F.). When cooled it solidifies in the form of plates or large broad needles, melting at – 10°·5 (13°·1 F.).

Heptylates.—The *baric salt* crystallizes from a hot concentrated solution in small very thin anhydrous plates; 100 pts. of a solution saturated at 12° (53°.6 F.) contain 1·7 pts. of the salt. *Calcic heptylate,* $(C_6H_{13}.CO_2)_2Ca + OH_2$, forms very thin flat needles, soluble in about 100 pts. of cold water. *Argentic heptylate* crystallizes in small woolly needles, sparingly soluble in hot water. A number of other salts have been described by Grimshaw and Schorlemmer.

By the action of sodium on ethylic acetate, and then of the iodide from fermentation amylic alcohol on the product, Frankland and Duppa obtained an isopentyl (amyl) acetic acid, but its properties have not been described.

Schneider has described (*Ann. Chem. Pharm.*, clvii. 206) under the name of *amethenic acid* an acid of the formula $C_7H_{14}O_2$, obtained by oxidation of diamylene (1237); it exhibits but feeble acid properties, and furnishes ill-characterized salts. Butlerow has suggested (*ibid.*, clxxiii. 375) that it is the tertiary heptylic acid, *dimethisopropacetic acid,* $(CH_3)_2CH.C(CH_3)_2.COOH$.*

(1730) Octylic or Caprylic Acids: $C_8H_{16}O_2$.—Only two of these acids are known. *Normal (primary) octylic acid,* $CH_3.(CH_2)_6.COOH$, is obtained by oxidation of normal primary octylic alcohol; it occurs as glyceric salt in cocoa-nut oil, butter, and other vegetable fats, and is a product of the oxidation of oleic acid and other fatty substances. It is best prepared by saponification of cocoa-nut oil. Octylic acid crystallizes in needles or plates, melting at 16°·5 (61°·7 F.); it boils at about 236° (456°·8 F.). It possesses a faint unpleasant odour, and sharp rancid taste; it is difficultly soluble even in hot water, from which it crystallizes in plates easily soluble in alcohol and benzene.

Baric octylate crystallizes in anhydrous plates; it dissolves only to the extent of 6 pts. in 100 pts. of water at 20° (68° F.).

Calcic octylate, $(C_7H_{15}.CO_2)_2Ca + OH_2$, crystallizes in long thin needles, less soluble in water than the baric salt. *Zincic* octylate forms anhydrous plates, melting at 136° (276°·8 F.). A number of other salts have been prepared, those containing heavy metals all have definite melting points, and although almost insoluble in water, like the preceding they are more or less soluble in alcohol (Zincke, *Ann. Chem. Pharm.*, clii. 1; Renesse, *ibid.*, clxxi. 380).

The only other octylic acid known is the isosecondary acid of the formula $C(CH_3)_3.CH_2.CH(CH_3).COOH$, obtained by oxidation of diisobutylene and of the carbinol *diisobutol* formed from this olefine.† It is an oily liquid, similar in odour to trimethacetic acid; it boils irregularly at 205°—218° (401°—424°.4 F.), and apparently decomposes partially on distillation. Its silver salt crystallizes in groups of small opaque needles; its cadmic salt is only slightly soluble in water (Butlerow, *ibid.*, clxxxix. 70).

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* The amylene obtained by the action of zincic chloride on fermentation amylic alcohol, according to the latest researches (*Deut. chem. Ges. Ber.*, ix. 1028; x. 81, 230, 404, 1904), appears to be a mixture of no less than four isomerides, viz., of $CH_3.CH{=}C(CH_3)_2$, $C_2H_5.C(CH_3){=}CH_2$, $(CH_3)_2CH.CH{=}CH_2$ and $C_2H_5.CH{=}CH.CH_3$ or $C_3H_7^{\alpha}.CH{=}CH_2$, and doubtless therefore diamylene is also a mixture; if, as is probable, it chiefly consists of *a*-diisopropyldimethylethylene, the formation of an acid of the kind suggested by Butlerow involves the occurrence of isomeric change. It appears possible that the olefine may be first converted into the oxide $\left.\begin{matrix} C_3H_7^{\beta}.C(CH_3) \\ C_3H_7^{\beta}.C(CH_3) \end{matrix}\right\} O$, which undergoing isomeric change is converted into the ketone $(CH_3)_2C(C_3H_7^{\beta}.)CO.C_3H_7^{\beta}$, and that the acid is formed by oxidation of this ketone.

† Diisobutylene is obtained either by heating trimethylcarbinol with dilute sulphuric acid, or a solution of isobutylene in the dilute acid, at 100° (212° F.)

(1731) NONYLIC ACIDS: $C_9H_{18}O_2$.—Two nonylic acids are known. *Normal primary nonylic acid*, $CH_3.(CH_2)_7.COOH$, is formed by displacing the OH group in normal primary octylic alcohol by COOH, and by oxidation of methylnonylketone, the chief constituent of oil of rue; it would appear probable also that the nonylic acid obtained by Redtenbacher by oxidizing oleic acid with nitric acid is the normal acid. The leaves of the geranium (*Pelargonium roseum*) are supposed to contain an acid of the formula $C_9H_{18}O_2$; and hence it has received the name pelargonic acid. Pure nonylic acid is crystalline, melting at about 12°·5 (54°·5 F.); it boils at about 254° (489°·2 F.).

Baric nonylate forms silky anhydrous plates, very difficultly soluble in cold water. *Calcic nonylate* is also anhydrous, and crystallizes from alcohol in thin silky plates. The cadmic and cupric salts may be crystallized from alcohol and exhibit constant melting points (Zincke and Franchimont, *ibid.*, clxiv. 333).

Isoprimary nonylic acid or *methhexacetic acid*, $C_6H_{13}.CH(CH_3).COOH$, is obtained from methylhexylcarbinol (from castor oil) by displacing the OH group by COOH. It is a colourless oil, insoluble in water, which remains liquid at − 11° (12°·2 F.), and boils at about 245° (473° F.). Its calcic salt $(C_8H_{17}.CO_2)_2Ca + OH_2$, is almost insoluble in water, but crystallizes from alcohol in fine needles (Kullhem, *ibid.*, clxxiii. 319).

(1732) HIGHER HOMOLOGUES OF ACETIC ACID.—A number of higher terms of the series have been obtained, mostly from natural fatty substances, in which they occur as glycerides, no term having more than a single representative, however. It appears probable that those containing 10 atoms of carbon and upwards are all normal acids, as they furnish lower normal acids of the series on oxidation, but there is no other evidence as to their constitution, and it is even doubtful whether several of them have been obtained in a pure state. They are crystalline, faintly acid bodies, insoluble in water, but soluble in alcohol and ether; their alkali-metal salts are readily soluble in water, but either do not crystallize, or crystallize with difficulty, and

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for several hours; its formation may be supposed to be the result of the action upon each other of two mols. of hydric tertiary-butylic sulphate, thus: $(CH_3)_3C.SO_4H + (CH_3)_3C.SO_4H = (CH_3)_3C.CH{=}C(CH_3)_2 + {}_2H_2SO_4$. It is a colourless mobile liquid, of the sp. gr. ·734 at 0° (32° F.); it boils at 102°·5 (216°·5 F.). By combining it with hydriodic acid, and decomposing the resulting iodide with argentic hydrate, the alcohol (*diisobutol*) $(CH_3)_3C.CH_2.C(CH_3)_2.OH$, is produced; it is a colourless liquid of camphorous odour, boiling at about 147° (296°·6 F.). Both the olefine and the alcohol furnish the same products on oxidation; apparently they are in the first instance chiefly resolved into trimethacetic acid and dimethylketone, but the latter is at once further oxidized; the above-mentioned octylic acid and the ketone $(CH_3)_3C.CH_2.CO.CH_3$ are also obtained in small quantity, being probably formed somewhat in the same manner that isobutyric acid is on oxidation of trimethylcarbinol (comp. p. 440).

are mostly partially decomposed by water, dissolving in a small quantity of water to form a clear solution, but in a large quantity of water to form a turbid alkaline solution, which lathers when shaken: octylic and nonylic acids in this respect resemble their higher homologues. The salts of other metals are mostly either very difficultly soluble or insoluble in water, but are generally more or less soluble in alcohol.[*]

In the following paragraphs only a very brief account of the remaining higher homologues of acetic acid will be given. For full details of the manner of preparing them and an account of their properties, the student is referred to Watts' *Dictionary* and to the original memoirs, especially to those of Heintz on the various animal fats (*Ann. Chem. Pharm.*, lxxxiv. 297; lxxxviii. 295, 300; xcii. 290; xcvii. 271); and to Brodie on wax (*Phil. Trans.*, 1848, 147; 1849, 91).

(1733) DECYLIC or CAPRIC ACID; *Rutic Acid;* $C_{10}H_{20}O_2 = C_9H_{19}.COOH$, occurs as glyceric salt in small quantity in butter and in cocoa-nut oil, and is formed together with several of the homologous acids of the series on oxidation of oleic acid by nitric acid. According to Rowney, it may be obtained in considerable quantity from the fusel oil of the Scotch whisky distilleries, and according to Fischer and Grimm it is also contained in wine fusel oil; apparently it is present in these oils as ethylic and amylic salts, associated with a relatively small quantity of the corresponding caprylates (*Ann. Chem. Pharm.*, lxxix. 236; cxviii. 312; clvii. 264). Capric acid has a faint goat-like odour; it is only slightly soluble in water, but readily dissolves in alcohol and ether, from which it crystallizes in brilliant plates, melting at 30° (86° F.); it boils at 268°—270° (514°·4—518° F.) with but little alteration (Grimm). *Baric caprate* crystallizes in brilliant anhydrous plates, difficultly soluble even in boiling water. The calcic salt yields the corresponding ketone $(C_9H_{19})_2CO$, when submitted to dry distillation (Grimm).

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[*] Most natural products which furnish higher acids of the acetic series furnish a mixture of these acids; in separating them, advantage is taken of the diminution in solubility of the salts which takes place as the molecular weight increases. Usually the mixture is dissolved in alcohol, and an alcoholic solution of magnesic or plumbic acetate is added so as to fractionally precipitate the acids; the earlier precipitates thus obtained consist chiefly of the acids of higher molecular weight, and the later precipitates of those of lower molecular weight, and by similarly treating the mixtures of acids separated from the various precipitates, and repeating these processes a sufficient number of times, the constituents of the mixture may eventually be isolated, although at a great expense of time, labour, and material. The lower terms of the series may be separated in a similar manner by means of the silver salts, but a more satisfactory method is to neutralize the mixture and to add sufficient sulphuric or hydrochloric acid to liberate only a portion of the organic acid, which is then distilled off, a fresh portion of acid added, and the liberated organic acid distilled off, and so on. The acids of higher molecular weight being the weaker are first liberated, and by properly adjusting the amount of acid added, and, if necessary, neutralizing the distillates and treating them in a similar manner, the presence of several volatile fatty acids in a mixture may, without great difficulty, be established. From a mixture of volatile acids, that of highest molecular weight passes over first on distillation, and this property also affords a means of separating the homologous acids (comp. Fitz, *Deut. chem. Ges. Ber.*, xi., 44.)

(1734) LAURIC ACID: $C_{12}H_{24}O_2 = C_{11}H_{23}.COOH$, occurs as glyceric salt in the fat from the berries of the bay-tree (*Laurus nobilis*) and from pichurim beans; it has also been obtained in small quantity from cocoa-nut oil, spermaceti, and a number of other fatty substances. It is insoluble in water, but crystallizes from alcohol or ether in white silky needles melting at 43°·6 (110°·5 F.); it partially decomposes on distillation. Its calcic salt is said to yield the corresponding ketone on distillation.

(1735) MYRISTIC ACID: $C_{14}H_{28}O_2 = C_{13}H_{27}.COOH$.—The glyceric salt of this acid is contained in the fat of the nutmeg (*Myristica fragrans*) and other species of myristiceæ, and is especially abundant in dika-bread, the fruit of the *Mangifera gabonensis*, a tree growing on the west coast of Africa. Myristic acid has also been obtained from many other fats, as butter, cocoa-nut oil, and spermaceti, which, however, yield it only in small quantity. It is insoluble in water and ether, but soluble in alcohol, from which it crystallizes in shining laminæ, melting at 53°·8 (128°·9 F.). It partially decomposes on distillation. Its calcic salt is said to yield the corresponding ketone on distillation.

(1736) PALMITIC ACID: $C_{16}H_{32}O_2 = C_{15}H_{31}.COOH$.—The normal glyceric salt of this acid is a constituent of most natural fats. In the more solid animal fats it is chiefly associated with glyceric stearate, whilst the vegetable oils chiefly contain glyceric oleate in addition; the solid portion of palm oil, the produce of *Elæis guianensis*, consists chiefly of glyceric palmitate. Palmitic acid also occurs as cetylic salt in spermaceti, and as cerylic salt in bees'-wax; its potassic salt is produced together with that of acetic acid when oleic acid is fused with potassic hydrate. It may be prepared by saponifying the solid portion of palm oil by boiling it with a solution of potassic or sodic hydrate, decomposing the resulting soap with sulphuric or hydrochloric acid, and repeatedly crystallizing the separated fatty acid from alcohol until it exhibits a constant melting point.

Palmitic acid is a tasteless odourless substance, insoluble in water, but it readily dissolves in hot alcohol or ether, yielding acid solutions; it crystallizes from dilute solutions in tufts of slender needles, melting at 62° (143°·6 F.); the fused acid solidifies to a mass of nacreous laminæ on cooling. It may be distilled almost without change. The normal palmitates of potassium and sodium readily dissolve in a small quantity of hot water, forming solutions which gelatinize on cooling; they are also freely soluble in hot alcohol, crystallizing from the solution on cooling in nacreous laminæ. On adding water to their concentrated aqueous solutions, crystalline hyperacid salts, such as the salt $KC_{16}H_{31}O_2.C_{16}H_{32}O_2$, corresponding to the hyperacid acetates, are precipitated. The salts of other metals are insoluble, and are obtained from those of the alkali-metals by double decomposition. The calcic salt furnishes the ketone $(C_{15}H_{31})_2CO$ on dry distillation; this crystallizes in pearly scales or laminæ, melting at 84° (183°·2 F.); on oxidation with chromic acid liquor, it appears to yield chiefly myristic acid together with lower acids of the series (Hercz, *Ann. Chem. Pharm.*, clxxxvi. 266).

(1737) MARGARIC ACID: $C_{17}H_{34}O_2 = C_{16}H_{33}.COOH$, is not known to occur naturally, the so-called margaric acid obtained from natural fats having been shown by Heintz to be a mixture of stearic acid with other lower acids of the series, chiefly palmitic acid; it has, however, been prepared by displacing the OH group in cetylic alcohol (1453) by COOH in the usual manner (Heintz

Pogg. Ann., cii. 272). The acid thus produced closely resembles palmitic acid, but melts at 69°·9 (157°·8 F.).

(1738) STEARIC ACID: $C_{18}H_{36}O_2 = C_{17}H_{35}.COOH$.—This acid occurs as glyceric salt in most fats and oils, being especially abundant in the more solid fats, such as beef and mutton suet. The so-called stearin, used in the manufacture of stearin candles, is a mixture chiefly of palmitic and stearic acids, prepared by pressing the mixture of acids obtained from the harder animal fats first in the cold and then at temperatures up to 30°—40° (86°—104° F.), in order to remove oleic acid and acids of low melting point. Pure stearic acid is best prepared from this mixture by dissolving 4 pts. of it in such a quantity of alcohol that nothing will separate out on cooling even to 0° (32° F.), and adding a boiling alcoholic solution of 1 pt. magnesic acetate to the hot liquid; the magnesic salt which separates on cooling is pressed, and then decomposed by boiling it for some time with a considerable quantity of dilute hydrochloric acid, and the still impure stearic acid thus obtained is repeatedly crystallized from alcohol until it exhibits a constant melting point.

It crystallizes in nacreous laminæ or needles, melting at about 69° (615°·2 F.); mixtures of stearic acid with another solid acid of the series, however, fuse, not at the medium fusing point, but mostly at lower temperatures, often even below that of the more fusible acid. A large number of observations on this subject have been made by Heintz. Stearic acid expands very strongly when heated, especially at the moment of fusion. It may be distilled unchanged under reduced pressure, or in a current of steam heated to 250°—350° (482°—662° F.), and even if distilled under the ordinary pressure it is for the most part unaltered, the small quantity which is decomposed yielding apparently lower acids of the series and ketones; but when several times distilled under pressure in a closed tube it is entirely decomposed, yielding water, CO_2 and a complex mixture of corresponding hydrocarbons of the paraffin and olefine series from the lowest term upwards to $C_{18}H_{38}$ and $C_{18}H_{36}$ (Johnston, *Jour. Chem. Soc.*, xxix. 8). Stearic acid appears to furnish chlorinated derivatives when submitted to the prolonged action of chlorine at 100° (212° F.); on oxidation with nitric acid, lower acids of the series and acids of the succinic series are said to be formed. The normal stearates of alkali-metals, like the corresponding palmitates, are soluble in water and alcohol, crystallizing from the latter; they are decomposed by a large quantity of water with formation of hyperacid salts. The stearates of other metals are mostly insoluble. Calcic stearate is said to furnish the corresponding ketone on dry distillation.

(1739) ARACHIDIC ACID: $C_{20}H_{40}O_2 = C_{19}H_{39}.COOH$.—The glyceric salt of this acid occurs in oil of earth-nut, the produce of *Arachis hypogæa*, a leguminous creeping plant, indigenous to India and the coasts of South Africa and South America. Arachidic acid crystallizes from alcohol in very small shining scales, melting at 75° (167° F.) (Görsmann, *Ann. Chem. Pharm.*, lxxxix. 1; xcvii. 257).

(1740) BEHENIC ACID: $C_{22}H_{44}O_2 = C_{21}H_{43}.COOH$.—The glyceric salt of this acid is said to occur in the oil expressed from the fruit of *Moringa nux behen*. The acid itself is a crystalline substance, melting at 76° (168°·8 F.).

(1741) HYÆNIC ACID: $C_{25}H_{50}O_2 = C_{24}H_{49}.COOH$.—According to Carius (*ibid.*, cxxxix. 168), this acid is present as glyceric salt in the fatty substance contained in the glandular pouches of the striped hyæna (*Hyæna striata*). It is said to resemble cerotic acid in its properties, and to melt at about 177° (350°·6 F.).

(1742) CEROTIC ACID: $C_{27}H_{54}O_2 = C_{26}H_{53}.COOH$, is the essential constituent of the portion of bees'-wax which is soluble in boiling alcohol; it also exists as cerylic cerotate in Chinese wax, and may be formed by oxidation of cerylic alcohol (1453), by fusion with potassic hydrate. It crystallizes from alcohol in small grains, melting at 78° (172°·4 F.); the pure acid distils without alteration. By exposing the melted acid to the action of chlorine for several days a chloro-acid of the formula $C_{27}H_{42}Cl_{12}O_2$ is formed.

(1743) **Melissic Acid**: $C_{30}H_{60}O_2 = C_{29}H_{59}.COOH$, is obtained by oxidation of myricylic alcohol (1853) by heating it with potash-lime. It closely resembles cerotic acid, but melts at about 89° (192°·2 F.).

In the following table the various homologous and isomeric acids of known boiling point are arranged in four groups of normal primary, isoprimary, secondary, and tertiary acids. On comparing the boiling points of the strictly homologous acids in

CH_2O_2	H $\vert$ COOH B.P. 100°			
$C_2H_4O_2$	CH_3 $\vert$ COOH B.P. 118°			
$C_3H_6O_2$	C_2H_5 $\vert$ COOH B.P. 140°·7			
$C_4H_8O_2$	$C_3H_7^{\alpha}$ $\vert$ COOH B.P. 162°·4		$CH(CH_3)_2$ $\vert$ COOH B.P. 154°	
$C_5H_{10}O_2$	$C_4H_9^{\alpha}$ $\vert$ COOH B.P. 185°	$CH_2.C_3H_7^{\beta}$ $\vert$ COOH B.P. 175°	$CH\begin{cases}CH_3\\C_2H_5\end{cases}$ $\vert$ COOH B.P. 173°	$C(CH_3)_3$ $\vert$ COOH B.P. 163°·8
$C_6H_{12}O_2$	$C_5H_{11}^{\alpha}$ $\vert$ COOH B.P. 205°	$CH_2.CH_2.C_3H_7^{\beta}$ $\vert$ COOH B.P. 199°	$CH(C_2H_5)_2$ $\vert$ COOH B.P. 196°	$C(CH_3)_2(C_2H_5)$ $\vert$ COOH B.P. 187°
$C_7H_{14}O_2$	$C_6H_{13}^{\alpha}$ $\vert$ COOH B.P. 224°			
$C_8H_{16}O_2$	$C_7H_{15}^{\alpha}$ $\vert$ COOH B.P. (?) 236°			$CH\begin{cases}CH_3\\CH_2.C(CH_3)_3\end{cases}$ $\vert$ COOH B.P. about 213°
$C_9H_{18}O_2$	$C_8H_{17}^{\alpha}$ $\vert$ COOH B.P. 254°		$CH\begin{cases}CH_3\\C_6H_{13}^{\alpha}\end{cases}$ $\vert$ COOH B.P. 245°	
$C_{10}H_{20}O_2$	$C_9H_{19}^{\alpha}$ $\vert$ COOH B.P. 268°—270°			

the first group, it will be seen that the difference between the successive terms in the case of the second, third, fourth and fifth members is approximately equal, being about 22° C.; the difference between successive terms then diminishes, but the differences are so irregular that it appears probable that the boiling points of the lower terms have been incorrectly determined. The terms in the other series are too few to admit of comparison.

(1744) *Ethereal Salts derived from Acids of the Acetic Series.*—1. The acids of the acetic series enter directly into reaction with many alcohols of various degrees of hydricity to form normal and basic ethereal salts, the change taking place in many cases even at ordinary temperatures; thus:

$$\underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Ethylic alcohol.}}{C_2H_5.OH} = \underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + OH_2.$$

$$\underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3} = \underset{\text{Glyceric monacetate.}}{CH_3.COOC_3H_5(OH)_2} + OH_2.$$

$$\underset{\text{Acetic acid.}}{2CH_3.COOH} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3} = \underset{\text{Glyceric diacetate.}}{(CH_3.COO)_2.C_3H_5(OH)} + 2OH_2.$$

Water being, however, a product of the reaction, the "etherification" is never complete in consequence of the occurrence of the reverse change; for example:

$$\underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + OH_2 = \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Ethylic alcohol.}}{C_2H_5.OH}.$$

The extent to which these opposite reactions take place, and hence the amount of ethereal salt formed, as well as the degree of rapidity with which it is produced, appear to vary according to the nature of the reacting substances, the relative amounts employed, the temperature to which the mixture is heated, and the time during which it is heated. Berthelot and Pean de St. Gilles, from a series of experiments with acetic acid and several primary alcohols of the ethylic series, came to the conclusion that the amounts of ethereal salt produced on heating mixtures of the various alcohols with acetic acid in simple molecular proportions, and also the rapidity with which the reactions took place, varied only within very narrow limits. The more extended series of observations recently published by Menschutkin (*Deut. chem. Ges. Ber.*, x. 1728, 1898), however, show that this is not the case, the discrepancy between his results and those of the before-named observers being apparently due to the fact that the latter did not continue the heating sufficiently long. The method employed by Menschutkin consisted in heating mixtures in as nearly as possible simple molecular proportions of the carefully purified alcohol and acetic acid in closed tubes of 1 c.c. capacity more than half filled with the mixture; the heating being effected in a bath of glycerol maintained as constantly as possible at a temperature of 153°—154° (307°·4—309°·2 F.). The amount of change taking place in a given time was ascertained by taking the tubes from the bath, cooling them quickly, and determining the residual acid in the mixture by titration with a solution of baric hydrate.

The *initial rate of change*, that is to say, the percentage of acid converted into ethereal salt in the first hour, and the *limit of change* or greatest percentage of acid ultimately converted into ethereal salt by prolonged heating, for a number of primary alcohols, are given in the following table:

Name of ethereal salt formed.	Initial rate of change.	Limit of change.
Methylic acetate	57·25	71·45
Ethylic „	46·60	69·61
Propylic „	46·39	70·90
Isobutylic „	45·40	73·46
Normal octylic „	46·56	82·24
Cetylic „	...	87·17 {probably higher.
Allylic „	36·80	61·88
Benzylic „	37·77	63·97
Cinnamic „	37·21	64·58

In considering the rate at which etherification takes place, Menschutkin distinguishes the absolute from the relative rate: the *absolute rate* being expressed by the proportion which the amount of acid or alcohol entering into reaction bears to the whole amount employed; and the *relative rate* by the proportion it bears only to the amount which can take part in the reaction, that is to say, to the limit of change. Methylic alcohol is sharply distinguished from its homologues by its high initial rate (absolute rate = 57·25; relative rate = 80·1); the three strictly homologous alcohols, ethylic, normal propylic and normal octylic alcohols etherify at the same initial rate, but apparently isoprimary butylic alcohol is attacked at a slightly lower rate; as the heating is continued, however, the alcohols of higher molecular weight appear to enter into reaction to a greater extent than those of lower molecular weight, so that it may be concluded that the rate at which the primary alcohols of the ethylic series enter into reaction with acetic acid increases with increase of molecular weight. Thus:

	1 hour.	2 hours.	4 hours.	7 hours.	48 hours.
Ethylic alcohol .	46·60	56·22	63·26	65·28	66·98
Propylic „ . . .	46·39	56·62	62·83	67·35	69·13
Isobutylic „ . . .	45·40	55·95	62·68	66·19	71·0
Octylic „ . . .	46·56	57·78	65·08	68·53	80·65

The relative initial rate, however, diminishes in a regular manner with increase of molecular weight, the diminution being about 1·8 per cent. for each additional atom of carbon in the case of the normal primary alcohols; thus:

	Found.	Calculated.
Ethylic alcohol	66·94	67·0
Propylic „	65·43	65·2
Isobutylic „	61·80	63·4
Octylic „	56·61	56·2

Isoprimary butylic alcohol, it will be observed, in this respect also behaves somewhat differently from the homologous alcohols. The relative rates of change on further heating appear also to diminish with increase of molecular weight, but the number of observations as yet made to determine this is few. If such be the case, however, the time required to attain the limit should be longer the higher the molecular weight of the alcohol; and actually it is found to be so, methylic alcohol attaining the limit after between 48 and 72 hours, ethylic alcohol after 72 hours, and propylic, isobutylic and octylic alcohol only after 96 hours. From ethylic alcohol upwards the limit appears to increase in a regular manner by about 2 per cent.; the limit for cetylic alcohol is lower than that calculated on this assumption, but Menschutkin is inclined to regard the value at present assigned to it as too low.

The unsaturated primary alcohols examined differ very slightly in their initial rates, but the absolute rate at which etherification takes place is considerably lower (by about 10 per cent.) than for the saturated alcohols; thus:

	Absolute.	Relative.
Allylic alcohol	36·80	59·40
Benzylic "	37·77	59·04
Cinnamic "	37·21	57·61

The secondary alcohols of the ethylic series, however, exhibit still lower absolute initial rates:

Dimethylcarbinol	25·72
Methylethylcarbinol	22·62
Methylisopropylcarbinol	19·62
Methylbutylcarbinol	19·13
Methylhexylcarbinol	19·38

But it will be observed that whereas in the case of the primary alcohols only methylic alcohol is etherified with greater rapidity than any other, in the case of these secondary alcohols, the first two terms are more rapidly acted on than any of the higher homologues. Again, whereas with the primary alcohols the absolute rate of change is nearly the same for the various homologues during the earlier hours, and increases only after some considerable time with increase of molecular weight, the secondary alcohols, which enter into reaction at the same initial rate, very soon manifest different rates; the rates at which change takes place during the second and later hours being in all cases absolutely greater for the secondary alcohols than for the corresponding primary. For example, in the first two hours 56·65 per cent. of propylic and 36·90 per cent. of isopropylic alcohol are etherified; during the first hour, however, 46·39 per cent. of propylic and 25·72 per cent. of isopropylic alcohol enter into reaction with the acid, whereas during the second 10·23 per cent. of propylic and 11·18 per cent. of isopropylic alcohol are converted into ethereal salt. Again, in the first four hours the amount of propylic alcohol acted upon is 62·83, and of isopropylic 52·82 per cent.; but in the first two hours 56·65 and 36·90 per cent. respectively are etherified, so that in the following two hours only 6.21 per cent. of the normal alcohol is converted into ethereal salt, the amount of secondary alcohol changed being three times as great (15·92 per cent). Although the rates of change during the earlier hours are greater for the secondary alcohols of lower molecular weight, as the heating is continued their rates of change become less, while those of higher mol. wt. enter to a greater extent into reaction with the acid, and, after heating about 36 hours, about equal amounts of all the various alcohols are converted into ethereal salts. From this point the law is the same as for the primary alcohols, the rate of change increasing with increase of molecular weight. The absolute amount of secondary alcohol which can be converted into ethereal salt by continued heating increases by about 1·1 per cent. for each additional atom of carbon, being a less difference than obtains in the case of the corresponding primary alcohols, of which also a considerably larger amount can be converted into ethereal salt, thus:

	Found.	Calculated.
Dimethylcarbinol	61·50	61·5
Methylethylcarbinol	62·43	62·6
Methylisopropylcarbinol	64·0	63·7
Methylbutylcarbinol	65·74	64·8
Methylhexylcarbinol	66·65	67·0

Two unsaturated secondary alcohols have been examined by Menschutkin—methylvinylcarbinol and diallylcarbinol. They differ from the saturated alcohols containing the same number of carbon atoms in a similar manner, but to a less extent, that the unsaturated differ from the saturated primary alcohols, the absolute initial rate of change being 15·32 per cent. for methylvinylcarbinol and 11·03 per cent. for diallylcarbinol, the relative rates being 27·52 and 20·49 per cent., and the limit of change 55·65 per cent. of the former and 53·66 per cent. of the latter.

Very little is known of the behaviour of the homologues of acetic acid and other acids, and alcohols other than those mentioned above. The results obtained by Berthelot and de St. Gilles (*Ann. Chim. Phys.*, [3], lxv. 385; lxvi. 5; and lxviii. 225), indicate, however, that the rate at which the homologous acids of the acetic series form ethereal salts diminishes with increase of mol. wt., and also that in the case of isologous acids, such as benzoic acid, they undergo etherification less rapidly than acetic acids.

2. Ethereal salts are readily produced by the action of the acid halides, and especially of the acid chlorides, on the alcohols; for example:

$$\underset{\text{Acetic chloride.}}{CH_3.COCl} + \underset{\text{Ethylic alcohol.}}{C_2H_5.OH} = \underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + HCl.$$

In this manner almost the theoretical amount of ethereal salt may be obtained.

3. A common method of preparing ethereal salts is to saturate a mixture of the given alcohol and acid with hydrochloric acid gas, the reaction being completed if necessary by heating the mixture in the water bath; to purify the product, it is usually merely requisite to wash it with water, removing the last portions of acid by the addition of a little sodic carbonate, and then to dry and fractionally distil it. The amount of ethereal salt produced in this manner is considerably larger, and the reaction takes place with much greater facility, than when only the alcohol and acid act upon each other, although the whole of the acid and alcohol do not undergo conversion.

Friedel (*Compt. Rend.*, lxviii. 1557) has endeavoured to explain the influence of the haloid acid by the assumption that it converts the acid into the acid chloride and water, and that the former at the moment of formation reacts upon the alcohol; this explanation being based upon the observation that acetic chloride, $CH_3.COCl$, may actually be obtained by the action of hydrochloric acid gas on a mixture of acetic acid and phosphoric anhydride at a temperature of about 80° (176° F.), a change which Demole has recently shown may be realized even at 0° (32° F.) (*Deut. chem. Ges. Ber.*, x. 1790). But as Henry has pointed out (*ibid.*, x. 2041), there is good reason to doubt the correctness of this explanation. The formation of acetic chloride from acetic acid and hydrochloric acid in presence of phosphoric anhydride, indeed, is probably induced by virtue of an influence exercised by the latter analogous to that of carbon in the formation of silicic tetrachloride on passing chlorine over a mixture of silica and charcoal, for the haloid acids alone appear to be incapable of converting the carboxyl acids into the corresponding acid halide; it may be supposed that acetic and hydrochloric acids do not enter into reaction because the formation of the acid chloride involves a considerable expenditure of energy, but that it takes place in presence of phosphoric anhydride in consequence of the development of more than sufficient energy to cover this loss by the combination of the water (which is one of the products of the reaction since $CH_3.COOH + HCl = CH_3.COCl + OH_2$) with the phosphoric anhydride to form metaphosphoric acid. But even supposing the acid chloride to be formed in the manner supposed by Friedel, it would be in presence of both water and the alcohol, and experiment shows that the former would be first attacked. A more probable explanation is that the alcohol and carboxyl acid first form an ether-alcohol, just as water and the acid form an acidhydrol (foot-note, p. 823), and that this compound is converted into an unstable monochlorhydrin, which breaks up into the ethereal salt and hydrochloric acid; thus in the case of acetic acid and ethylic alcohol, the following reactions may be supposed to occur successively:

$$CH_3.CO(OH) + C_2H_5.OH = CH_3.C(OH)_2(OC_2H_5);$$
$$CH_3.C(OH)_2(OC_2H_5) + HCl = CH_3.CCl(OH)(OC_2H_5) + OH_2;$$
$$CH_3.CCl(OH)(OC_2H_5) = CH_3.CO(OC_2H_5) + HCl.$$

In place of hydrochloric acid, sulphuric acid may often be advantageously employed, the mixture of alcohol, carboxylic acid and this acid being warmed for some time in the water bath. Its action is doubtless similar to that of hydrochloric acid.

4. Another method frequently employed for the preparation of ethereal salts derived from acids of the acetic series and the lower alcohols of the ethylic series is to act upon a salt of the acid, usually the sodic salt, with an acid ethereal sulphate such as hydric ethylic sulphate; for example:

$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + \underset{\text{Ethylic hydric sulphate.}}{C_2H_5.HSO_4} = \underset{\text{Ethylic acetate.}}{CH_3.COOC_2H_5} + NaHSO_4.$$

5. The haloid derivatives of hydrocarbons, such as iodethane and *a*-dibromethane, for example, also enter into reaction with the metallic salts of acids, especially silver salts, in a similar manner; thus:

$$\underset{\text{Potassic acetate.}}{CH_3.COOK} + \underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} = \underset{\text{Bromethylic acetate.}}{CH_3.COOC_2H_5Br} + KBr.$$

$$\underset{\text{Argentic acetate.}}{2CH_3.COOAg} + \underset{\text{Ethylenic bromide.}}{C_2H_4Br_2} = \underset{\text{Ethylenic acetate.}}{(CH_3.COO)_2C_2H_4} + 2AgBr.$$

A very large proportion of the ethereal salts are liquids, chiefly those derived from polyhydric alcohols being solids; many of the former possess characteristic fruity odours. With few exceptions, they are either difficultly soluble or insoluble in water, but readily soluble in alcohol and ether. In contact with water at ordinary temperatures, they either remain unchanged or undergo decomposition only to a very slight extent, but they are more or less readily resolved into the alcohol and acid on heating with water, this change being greatly facilitated by the presence of a mineral acid or of an alkali; they are, however, much more readily acted upon by water than the ethers such as ethylic oxide $(C_2H_5)_2O$.

(1745) ETHEREAL SALTS DERIVED FROM THE ACIDS OF THE ACETIC SERIES AND MONOHYDRIC ALCOHOLS.—The following table is a list of the ethereal salts, at present known, derived from these acids and the alcohols of the ethylic series:

	B. P. ° C.	S. G. at 0° C.	Observer.
Methylic formate . .	33·4	·998	Kopp.
" acetate . .	56·3 53·0	·956 —	" Dittmar.
" butyrate . .	96	·909	Kopp.
" isobutyrate .	93	·905	Pierre and Puchot.
" isovalerate* .	116	·901	Kopp.
" trimethacetate	101	—	Butlerow.
" nonylate . .	214	·876 (17°·5)	Zincke and Franchimont.
" decylate . .	224	—	Grimm.
Ethylic formate . .	54·9 54·4	·944 —	Kopp. Dittmar.
" acetate . . .	74·3 77·0	·910 ·906 (15°)	Kopp. Linnemann.
" propionate . .	98·8	·8945 (17°)	"
" butyrate . .	121·0	·899 (17°)	"
" isobutyrate .	113	·890	Pierre and Puchot.
" valerate . .	145	·894	Lieben and Rossi.
" isovalerate . .	135·5	·886	Pierre and Puchot.
" trimethacetate	118·5	·875	Butlerow.
" caproate . .	167 166	·8765 (17°·5) ·890	Zincke and Franchimont. Lieben and Rossi.
" isocaproate* .	161	·887	" "
" heptylate . .	189·3 188	·888 ·8735 (16°)	Lieben and Janeck. Grimshaw & Schorlemmer.
" octylate . .	208	·873 (16°)	Zincke.
" nonylate . .	228	·8655 (17°·5)	Zincke and Franchimont.
" decylate .	(?) 243	—	Fischer.
Propylic formate . .	83	·920	Pierre and Puchot.
" acetate . .	103	·910	" "

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* The so-called isovalerates and isoamylic salts have all been prepared from fermentation amylic alcohol, and are therefore mixtures.

	B.P. °C.	S.G. at 0° C.	Observer.
Propylic propionate .	124·3	·903	Pierre and Puchot.
	122·4	·8885 (13°)	Linnemann.
„ butyrate . .	143·4	·879 (15°)	„
„ isobutyrate .	137·3	·888	Pierre and Puchot.
„ isovalerate* .	157	·887	„ „
Isopropylic acetate . .	90—93	—	Friedel.
„ butyrate .	128	·879	Silva.
„ isovalerate*	142	·870	„
Amylic acetate . . .	149	·896	Lieben and Rossi.
Isoamylic* formate .	116	·874 (21°)	Kopp.
„ acetate . .	140	·873 (15°)	Schorlemmer.
„ isobutyrate .	170·3	·877	Pierre and Puchot.
„ isovalerate*	190	·874	„ „
Secondary amylic acetate	134 (?)	·922	Wurtz.
Hexylic acetate . .	170	·889 (17°·5)	Franch. and Zincke.
„ caproate . .	245·6	·865 (17°·5)	„ „
Heptylic acetate . .	191·5	·874 (16°)	Cross.
„ heptylate . .	271	—	„
Octylic acetate . . .	207	·872 (16°)	Zincke.
„ isovalerate . .	250	·862 (16°)	„
„ octylate . .	298	·862 (16°)	„

Only a small number of ethereal salts derived from monohydric alcohols of other series are known. Allylic formate, according to Tollens, boils at 82°—83°, and at 17° has the sp. gr. ·932; and, according to Hofmann and Cahours, allylic acetate, butyrate, and isovalerate boil respectively at 98°—100°, 140°, 145°, and 162°. The acetate derived from allyldimethylcarbinol boils at 137°·5; and at 0° has the sp. gr. ·900 (M. and A. Saytzeff); while that formed from menthylic alcohol (1458) boils at 223°. The only ethereal salts of alcohols of the $C_nH_{2n-3}.OH$ series, at present known are propargylic acetate, which boils at 125°, and at 12° has the sp. gr. 1·003 (Henry); and the acetate formed from diallylcarbinol, which boils at 169°·5, and at 0° has the sp. gr. ·917. Phenylic acetate boils at (?) 190°, and benzylic acetate at 210°; a number of acetates derived from the homologous alcohols have already been referred to in describing the homologues of phenol.

(1746) ETHYLIC FORMATE; *Formic Ether:* $C_3H_6O_2 = H.COOC_2H_5$.—This salt may be formed by distilling a mixture of formic acid or sodic formate and ethylic alcohol with sulphuric acid; or by distilling a mixture of ethylic oxalate and anhydrous oxalic acid in simple molecular proportions: the acid oxalate formed by the interaction of these substances being resolved at the moment of formation into ethylic formate and carbonic anhydride: $COOH.COOC_2H_5 = H.COOC_2H_5 + CO_2$, and it is in virtue of the occurrence of this reaction that ethylic formate is obtained as a secondary product in the preparation of ethylic oxalate by distillation of a mixture of ethylic alcohol and oxalic acid.

Ethylic formate is a colourless mobile liquid, having an agreeable pungent odour, soluble in about 9 pts. of cold water; it is violently acted upon by chlorine, furnishing a series of substitution products. The action of sodic ethylate and of sodium on this salt and its homologues will be discussed later on.

(1747) METHYLIC ACETATE: $C_3H_6O_2 = CH_3.COOCH_3$.—This salt is a constituent of crude wood spirit; it may be prepared by distilling a mixture of 1 pt. acetic acid, 2 pts. methylic alcohol, and 1 pt. sulphuric acid, but unless the pure alcohol be employed, it is impossible to obtain it free from acetone. The pure salt may be conveniently obtained by distilling a mixture of pure methylic oxalate and glacial acetic acid with the addition of a small quantity of fuming hydrochloric acid (Dittmar).

It is a colourless liquid, having an agreeable odour, closely resembling ethylic acetate in all its properties. According to Dittmar's experiments (*Journ. Chem. Soc.*, xxi. 477) methylic acetate has a lower vapour tension than ethylic formate at temperatures between 18° and 80° C., the difference being greater the higher the temperature: the difference at 18° C., for example, being 15.3 mm., and at 78°·7 C. 60 mm. When submitted to the action of chlorine, methylic acetate furnishes a series of substitution derivatives, and apparently the whole of the hydrogen may ultimately be displaced. The first product has the formula $CH_3.COOCH_2Cl$; it has a pungent suffocating odour, and boils at 115° (239° F.), whereas methylic monochloracetate, $CH_2Cl.COOCH_3$, has a pleasant odour and boils at 127° (260°·6 F.); it is rapidly decomposed in contact with cold water, forming acetic and hydrochloric acids and apparently methaldehydrol, $CH_2(OH)_2$; it is also readily acted upon by sulphuric acid, potassic acetate and ammonia (Henry, *Deut. chem. Ges. Ber.*, vi. 739). The second product of the action of chlorine has the formula $CH_3.COOCHCl_2$, as it yields formic and acetic acids when decomposed by water (Malaguti). The higher substitution derivatives have been very imperfectly examined. According to Grimaux (*Bull. Soc. Chem.*, xxii. 74) the pentachlorinated methylic acetate of Cloez, formed by the action of chlorine on citrates, and which is also said to be the final product of the action of chlorine on methylic acetate in the shade, is pentachloracetone, formed in the latter case, from the acetone present in the acetate; the same chemist has shown that the corresponding product of the action of bromine is pentabromacetone and not pentabrominated methylic acetate, and that bromine is without action on pure methylic acetate (comp. Steiner, *Deut. chem. Ges. Ber.*, vii. 1284).

(1748) **Ethylic Acetate**; *Acetic Ether*: $C_4H_8O_2 = CH_3.COOC_2H_5$.—This ethereal salt may be obtained by any of the general methods previously described, but it is usually prepared by distilling a mixture of ethylic hydric sulphate (sulphovinic acid) and sodic acetate. The following mode of proceeding is recommended by Frankland and Duppa (*Chem. Soc. Journ.*, xix. 396) when large quantities are required:—90 pts. of concentrated sulphuric acid are placed in a deep stoneware vessel and 36 pts. of 97 per cent. alcohol are allowed to flow into it by means of a piece of narrow glass tube, passing to the bottom of the vessel, and connected with a convenient reservoir standing at a considerable elevation; this tube is used as an agitator during the continuance of the flow of the alcohol, and in this way there is obtained, without loss of alcohol, a high temperature which greatly favours the formation of the sulphate. The mixture thus produced is allowed to stand twenty-four hours before use, and is then gradually poured over 60 pts. of previously dried and fused sodic acetate broken into small pieces and placed in a still immersed in cold water, care being taken that the temperature does not rise high enough to distil off any of the product; after standing about twelve hours, the mixture is submitted to distillation, and the product purified by rectification from powdered fused calcic chloride.

Ethylic acetate is a colourless mobile liquid, soluble in 11—12 pts. of cold water, and of sp. gr. ·906 at 15° (59° F.); it boils at 77° (170°·6 F.). When diluted with alcohol or water it has a very pleasant fruity odour, but the odour of the pure compound is less agreeable and extremely pungent. It slowly decomposes in contact with cold water, and is rapidly decomposed on heating with water or alkalies, with formation of ethylic alcohol and acetic acid or alkaline acetate; its decomposition by water, however, is not complete unless a large excess of the latter be employed at a relatively high temperature, the extent to which change takes place at lower temperatures depending on the temperature and the relative proportions of the reacting substances. Its decomposition by water is also facilitated by the presence of hydrochloric or sulphuric acid.

The chlorides of phosphorus are without action on ethylic acetate at its boiling-point, but it is readily attacked by chlorine with formation of substitution-compounds, and it is said that by continuing the action in bright sunlight the whole of the hydrogen may be displaced by chlorine; the resulting compounds have been but very imperfectly examined, however. According to Schützenberger, slight heat is developed on mixing bromine with ethylic acetate, and if a current of dry air be passed through mixtures of the two substances, whatever the proportions, a residue is finally obtained of the composition, $C_4H_8O_2Br_2$. By heating a mixture of bromine and ethylic acetate in simple molecular proportions in sealed tubes at 150° (302° F.), bromacetic acid is produced in accordance with the equation: $CH_3.COOC_2H_5 + Br_2 = CH_2Br.COOH + C_2H_5Br$ (Crafts); if double this quantity of bromine be employed and the mixture be heated to 120°—130° (248°—266° F.), dibromacetic acid is formed (Carius, *Deut. chem. Ges. Ber.*, iii. 336): $CH_3.COOC_2H_5 + 2Br_2 = CHBr_2.COOH + C_2H_5Br + HBr$. (comp. Hell, *ibid.*, xi. 245).

(1749) HALOGEN SALTS OF THE ACIDS OF THE ACETIC SERIES.—These salts, which were discovered by Schützenberger in 1861 (for a full description, see *Leçons professées en* 1868 *et* 1869 *devant la Société Chimique de Paris*), are formed by the displacement of the hydrogen of the COOH group by the negative radicles Cl, Br and I; they are produced by methods precisely similar in principle to those involved in the formation of the metallic salts, although they cannot be prepared directly from the acids by the action of the halogens.

(1750) CHLORINE ACETATE: $C_2H_3ClO_2 = CH_3.COOCl$, is prepared by passing a current of hypochlorous anhydride into acetic anhydride cooled by water until the liquid acquires a marked yellow colour; the excess of hypochlorous anhydride is then expelled by carefully warming the solution to 30° (86° F.). The reaction which takes place is precisely analogous to that occurring in the formation of argentic acetate from acetic anhydride and argentic oxide:

$$\underset{\text{Acetic anhydride.}}{\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O} + Cl_2O = \underset{\text{Chlorine acetate.}}{2CH_3.COOCl.}$$

$$\underset{\text{Acetic anhydride.}}{\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O} + Ag_2O = \underset{\text{Argentic acetate.}}{2CH_3.COOAg.}$$

Thus prepared, chlorine acetate is a pale yellow-coloured liquid, possessing a powerful irritating odour; if heated above 100° (212° F.), it detonates violently, being resolved into carbonic anhydride and chloromethane: $CH_3.COOCl = CO_2 + CH_3Cl$. It gradually decomposes in a similar manner at the ordinary temperature. It dissolves in water in all proportions, but with decomposition, acetic and hypochlorous acids being produced. When brought into contact with metals, such as copper, zinc, mercury, potassium or sodium, it is at once decomposed, chlorine being evolved, and the corresponding metallic acetate formed:

$$2CH_3.COOCl + 2Na = 2CH_3.COONa + Cl_2.$$

Chlorine acetate at once unites with ethylene, and apparently with the homologous olefines, forming corresponding chloracetins; for this purpose it is conveniently employed diluted with an equal weight of acetic anhydride:

$$\underset{\text{Ethylene.}}{CH_2{=\!=}CH_2} + CH_3.COOCl = \underset{\text{Chlorethylic acetate.}}{CH_3.COO(CH_2.CH_2Cl)}.$$

(1751) Bromine Acetate: $C_2H_3BrO_2 = CH_3.COOBr$—On adding bromine to chlorine acetate, chlorine is disengaged, and the corresponding bromine salt is formed: $2CH_3.COOCl + Br_2 = 2CH_3.COOBr + Cl_2$. It apparently resembles chlorine acetate closely in its properties, but is a far less stable compound.

(1752) Iodine Triacetate: $C_6H_9O_6I = (CH_3.COO)_3I$.—On adding iodine to chlorine acetate, it immediately dissolves, chlorine being disengaged; and when sufficient iodine has been added, brilliant colourless crystals are deposited. The compound thus produced does not, however, strictly correspond in composition to chlorine acetate, but results from the displacement of 3 atoms of chlorine in 3 molecules of the latter by a single atom of iodine, and thus bears a relation to chlorine acetate similar to that which bismuthic nitrate, $Bi(NO_3)_3$, for example, bears to argentic nitrate, $AgNO_3$:

$$6CH_3.COOCl + I_2 = 2(CH_3.COO)_3I + 3Cl_2.$$

Its formation affords a most striking example of the tendency of iodine to act as a triad, a tendency whereby it is in a marked manner distinguished from chlorine and bromine.

Iodine triacetate is more readily prepared by passing hypochlorous acid gas into a mixture of about 50 grams acetic anhydride and 15—20 grams pure dry iodine, which is maintained at the ordinary temperature; the reaction is terminated when the effervescence due to the escape of chlorine ceases, and the liquid becomes decolorized and filled with a mass of small colourless coherent crystals. These crystals, which are extremely sensitive to the action of light, may be purified by decanting the mother-liquor, and recrystallizing from acetic anhydride, in which they may be dissolved by warming to about 60° (140° F.).

Iodine triacetate forms large colourless prisms, which at once become pink and then brown on exposure to light; it is decomposed by water with formation of acetic and iodic acids, and also by alcohol; ether and benzene dissolve it without change. When heated to about 140° (284° F.), it decomposes with almost explosive violence, forming carbonic anhydride, iodine, and methylic acetate.

Iodine triacetate may apparently also be formed by the action of iodine chloride on sodic acetate. In its preparation as above described, there is an intermediate compound first produced in accordance with the equation: $2Cl_2O + I_2 + 2(CH_3.CO)_2O = I(CH_3.CO_2)_2Cl + Cl_2$. This compound crystallizes in long yellow needles; by the action of chlorine acetate it is converted into iodine triacetate: $I(CH_3.COO)_2Cl + CH_3.COOCl = I(CH_3.COO)_3 + Cl_2$.

Butyric anhydride, if submitted to the action of hypochlorous anhydride or of hypochlorous anhydride and iodine, furnishes analogous compounds to the above described acetates.

(1753) Cyanogen Acetate.—When acetic chloride is allowed to act upon argentic cyanate, decomposition takes place in accordance with the equation: $CH_3.COCl + CNOAg = CH_3.COO(CN) + AgCl$, but the product is a solid substance, which is probably a polymeride of the compound, $CH_3.COONC$. On heating, it does not furnish a volatile product at 90° (194° F.), but below 100° (212° F.), a regular evolution of carbonic anhydride takes place, and a mobile pungent-smelling liquid distils over; the distillate is apparently a mixture of methylic cyanide, $CH_3.CN$, and the acetate $CH_3.COONC$, but the latter cannot be isolated by fractional distillation. The mixture boils at 80°—85° (176°—185° F.), and on treating it with water, effervescence takes place owing to the escape of carbonic anhydride, whilst acetamide is produced: $CH_3.COO(NC) + OH_2 = CH_3.CO(NH_2) + CO_2$ (Schützenberger, *loc. cit.*).

(1754) Thioacids of the Acetic Series.—*Thiacetic acid:* $C_2H_4OS = CH_3.CO.SH$.—These acids are formed by the displacement of one of the atoms of oxygen in the acids of the acetic series by sulphur, and are produced by the action of the sulphides of phosphorus on the latter; thiacetic acid is the only member of the group which has been investigated. It is best prepared by heating a mixture of 300 grams phosphorus pentasulphide and 108 grams acetic acid in a retort, which it as nearly as possible half fills, until reaction commences; the source of heat is then removed, and only that portion of the product which is volatilized by the heat developed in the reaction collected. This product is afterwards rectified. If the mixture be heated after the reaction has taken place, much of the thiacetic acid is decomposed by the action of the sulphur compounds present. Thiacetic acid may also be formed by the action of acetic chloride on potassic thiohydrate: $CH_3.COCl + KSH = CH_3.COSH + KCl$; by digesting phenylic acetate, $CH_3.COOC_6H_5$, with an alcoholic solution of potassic thiohydrate; and by the action of water on acetic disulphide, $(C_2H_3O)_2S_2$ (Kekulé; Kekulé and Linnemann, *Ann. Chem. Pharm.*, xc. 311; cxxiii. 273; Ulrich, *ibid.*, cix. 272).

Thiacetic acid is a colourless liquid of unpleasant odour, like that of acetic acid and hydric sulphide together; it boils at about 93° (199°·4 F.), but undergoes slight decomposition. It has the sp. gr. 1·074 at 10° (50° F.); is soluble in water and alcohol; and does not solidify when cooled to – 17° (1°·4 F.). Thiacetic acid furnishes a series of metallic salts analogous in composition to the corresponding acetates; the lead salt, $(CH_3.COS)_2Pb$, obtained by precipitating a solution of plumbic acetate with thiacetic acid, is one of the most characteristic: it crystallizes from hot water in colourless silky needles, which, however, soon blacken even in the dry state. The ethylic salt, obtained by the action of phosphorus pentasulphide on ethylic acetate, boils at about 80° (176°). Thiacetic acid is decomposed with explosive violence by warm nitric acid; when submitted to the action of chlorine gas, it yields acetic chloride, hydrochloric acid and sulphur chloride, and it is acted upon in a similar manner by phosphorus pentachloride; it is also decomposed by sulphuric acid. When it is mixed with aniline, a reaction soon takes place, sulphuretted hydrogen being evolved, and eventually a crystalline mass of acetanilide remains: $CH_3.COSH + C_6H_5.NH_2 = C_6H_5.NH(CH_3.CO) + SH_2$.

(1755) Acid Halides derived from the Acids of the Acetic Series.—These compounds are formed by the displacement of the group OH in the carboxyl group by halogens, and are produced by the action of the haloid phosphorus compounds on the acids themselves, their salts, or the corresponding anhydrides. The displacement of OH in the COOH group by halogens cannot be affected by the action of the haloid acids as in the case of the carbinols; acid chlorides may, however, be obtained by the action of hydrochloric acid on the acids in presence of a powerful dehydrating agent such as phosphoric anhydride.

The acid halides may also be regarded as formed from the aldehydes by the displacement of H in the group COH by a halogen, and several of them have been produced in this manner.

The acid halides are extremely active bodies, entering readily into reaction with a large number of other compounds, especially hydroxyl and amidogen derivatives; they are decomposed even by cold water: those of lowest molecular weight being most readily acted upon.

Acid halides derived from formic acid are unknown, this acid being completely decomposed by the haloid phosphorus compounds; thus: $H.COOH + PCl_5 = CO + 2HCl + POCl_3$.

(1756) ACETIC CHLORIDE; *Chloride of acetyl:* $CH_3.COCl$.—This compound is most readily prepared by adding phosphorus trichloride to acetic acid in proportions in accordance with the equation $3CH_3.COOH + PCl_3 = 3CH_3.COCl + H_3PO_3$, warming the mixture to complete the reaction and then distilling; the product merely requires a single rectification. It may be prepared in a similar manner with the aid of phosphorus pentachloride or oxychloride, or by the action of each of these three phosphorus compounds on the metallic acetates. The action of phosphorus pentachloride on acetic acid is expressed by the equation: $CH_3.COOH + PCl_5 = CH_3.COCl + POCl_3$; this reaction takes place with great readiness and may be effected entirely without the aid of heat, but a volatile phosphorus compound being formed, this method is less well adapted for the preparation of the pure chloride. When phosphorus oxychloride acts on a metallic acetate, such as sodic acetate, the following reaction occurs: $POCl_3 + 2CH_3.COONa = 2CH_3.COCl + NaCl + NaPO_3$.

Acetic chloride is also formed by the action of phosphorus pentachloride on acetic anhydride, $(CH_3.CO)_2O$; by the action of chlorine on acetaldehyde (comp. 1628) and by the action of hydrochloric acid in presence of phosphoric anhydride on acetic acid: this latter reaction takes place even at 0° (32° F.) (comp. Friedel, *Compt. Rend.*, lxviii. 1557; Demole, *Deut. chem. Ges. Ber.*, x. 1790).

Acetic chloride is a colourless, mobile, pungent-smelling liquid, of the sp. gr. 1.1305 at 0° (32° F.); it boils at 55° (131° F.). It fumes strongly in moist air, and is immediately decomposed with explosive violence when placed in contact with water.

ACETIC BROMIDE or *Bromide of acetyl:* $CH_3.COBr$, is prepared in a precisely similar manner by means of the bromides of phosphorus, and closely resembles the chloride, but boils at 81° (177°·8 F.).

ACETIC IODIDE or *Iodide of acetyl:* $CH_3.COI$, cannot be obtained by the action of phosphorus tri-iodide on acetic acid, but is produced by acting with this iodide on acetic anhydride (Guthrie, *Ann. Chem. Pharm.*, ciii. 335), or potassic acetate (Cahours, *Compt. Rend.*, xliv. 1252). According to Guthrie, iodine is gradually added to a mixture of acetic anhydride and a slight excess of phosphorus; the flask or retort containing the mixture is then heated for a short time to complete the reaction, after which the product is distilled off, violently shaken with mercury to remove iodine, and rectified. It boils at 108° (226°·4 F.), but is partially decomposed, and therefore cannot be obtained colourless in this manner; like the corresponding chloride and bromide, it is immediately decomposed by water. Attempts to prepare diacetyl from it by the action of metals have been unsuccessful: it is violently acted upon by finely-divided silver, and a liquid product is obtained which consists almost entirely of acetic acid and acetic anhydride, mixed, however, with a small quantity of an extremely pungent-smelling substance, which gradually decomposes on keeping, furnishing a black carbonaceous matter; a solid product is also formed, and remains mixed with the argentic iodide, which contains less hydrogen than acetic iodide and very little oxygen (Wislicenus and Ponamareff, *Deut. chem. Ges. Ber.*, iv. 525).

The acid halides homologous with those of acetic acid closely resemble these latter in their properties. The following are known:

		B. P. ° C.
Propionic chloride	$C_2H_5.COCl$	80
Propionic bromide	$C_2H_5.COBr$	97
Propionic iodide	$C_2H_5.COI$	128
Butyric chloride	$C_3H_7.COCl$	101
Isobutyric chloride	$(CH_3)_2CH.COCl$	92
Isovaleric chloride	$C_4H_9.COCl$	115
Trimethacetic chloride	$C(CH_3)_3.COCl$	—

(1757) ACETIC CYANIDE; *Acetyl cyanide:* $C_3H_3ON = CH_3.CO.CN$.—To prepare this compound, a mixture of acetic chloride and argentic cyanide in equivalent proportions is heated in sealed tubes for one or two hours at 100° (212° F.). It is a colourless liquid, lighter than water, smelling both of acetic and hydrocyanic acids; it boils at 93° (199°·4 F.). When brought into contact with water, it gradually dissolves in it, forming acetic and hydrocyanic acids. If it be preserved in a corked flask, or treated with solid potassic hydrate or with sodium, it is converted into an oil insoluble in water, which after a time becomes crystalline. This substance is also a product of the action of acetic chloride on argentic cyanide, and is polymeric with the liquid cyanide; its vapour density corresponds with the formula, $C_6H_6O_2N_2$. It melts at 69° (156°·2 F.), and boils at about 208° (406°·4 F.) (comp. Fileti, *Deut. chem. Ges. Ber.*, ix. 82); when heated with water in sealed tubes, or with concentrated sulphuric acid, it yields acetic and hydrocyanic acids (Hübner, *Ann. Chem. Pharm.*, cxx. 334; cxxiv. 315). According to Claisen and Shadwell (*Deut. chem. Ges. Ber.*, xi. 621), when well-cooled acetic cyanide is mixed with a quantity of highly concentrated hydrochloric acid containing exactly the amount of water required by the proportion $C_3H_3ON : OH_2$, a crystalline amide of the composition $C_3H_5O_2N$ is formed, which on digestion with dilute hydrochloric acid is converted into an acid of the composition $C_3H_4O_3$, closely agreeing in its properties with pyruvic acid (q. v.).

Isovaleric cyanide: $C_4H_9.CO.CN$.—By acting on isovaleric chloride with argentic cyanide, this cyanide is obtained as a colourless thick fluid boiling at 145°—150° (293°—302° F.) (Hübner, *ibid.*, cxxxi. 74).

(1758) ACID OXIDES OR ANHYDRIDES DERIVED FROM THE ACIDS OF THE ACETIC SERIES.—The anhydrides bear the same relation to the corresponding acids that the ethers or basic oxides, such as ethylic ether, bear to the corresponding monohydric alcohols; thus:

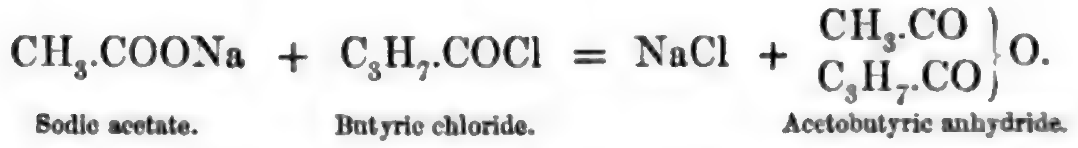
$C_2H_5.OH$;	$\left.\begin{array}{l}C_2H_5\\C_2H_5\end{array}\right\}O.$	$CH_3.CO(OH)$;	$\left.\begin{array}{l}CH_3.CO\\CH_3.CO\end{array}\right\}O.$
Ethylic alcohol.	Ethylic oxide. (Ethylic ether.)	Acetic acid.	Acetic oxide. (Acetic anhydride.)

They are chiefly distinguished from the ethers by the readiness with which they enter into reaction with water and basic oxides.

The anhydrides are usually prepared by the action of the acid chlorides on metallic salts of the acids, the sodic salts being most frequently employed. Reaction takes place at once on bringing the two compounds together, considerable heat being developed; to complete the reaction, the mixture is heated for a short time and then distilled. If the metallic salt and the acid chloride be derived from the same acid, a *simple* anhydride is produced; thus:

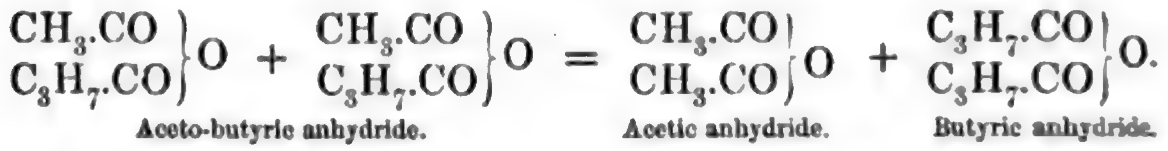
$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + \underset{\text{Acetic chloride.}}{CH_3.COCl} = NaCl + \underset{\text{Acetic anhydride.}}{(CH_3.CO)_2O.}$$

But if this be not the case, a *mixed* anhydride is formed:



$$\underset{\text{Sodic acetate.}}{CH_3.COONa} + \underset{\text{Butyric chloride.}}{C_3H_7.COCl} = NaCl + \underset{\text{Acetobutyric anhydride.}}{\left.\begin{matrix}CH_3.CO\\C_3H_7.CO\end{matrix}\right\}O.}$$

The mixed anhydrides may be separated from the metallic chloride by means of pure ether, but not by distillation, as they undergo decomposition when distilled, being resolved into a mixture of the two corresponding simple anhydrides; thus:



$$\underbrace{\left.\begin{matrix}CH_3.CO\\C_3H_7.CO\end{matrix}\right\}O + \left.\begin{matrix}CH_3.CO\\C_3H_7.CO\end{matrix}\right\}O}_{\text{Aceto-butyric anhydride.}} = \underset{\text{Acetic anhydride.}}{\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O} + \underset{\text{Butyric anhydride.}}{\left.\begin{matrix}C_3H_7.CO\\C_3H_7.CO\end{matrix}\right\}O.}$$

In preparing the simple anhydrides, it is not essential to first prepare the acid chloride in a pure state, and then to act upon the metallic salt with it; the two operations may be combined in one by acting upon the metallic salt of the acid with phosphoric oxychloride in the proportion of 4 mols. of the former to 1 of the latter. From one half of the metallic salt and the oxychloride there is formed the equivalent amount of acid chloride and a metallic metaphosphate, and the acid chloride thus produced then enters into reaction with the remaining portion of the metallic salt.

Simple anhydrides may also be prepared by digesting a mixture of an acid chloride and the corresponding acid in simple molecular proportions, as long as hydrochloric acid is evolved, the product being purified by fractional distillation; thus: $CH_3.COCl + CH_3.COOH = HCl + (CH_3.CO)_2O$. A modification of this method consists in adding phosphorus trichloride to the acid in the proportion of 1 mol. to 6 mols., the mixture being subsequently heated in a flask or retort attached to a reversed condenser until the evolution of hydrochloric acid is at an end, and then distilled.

The following simple anhydrides of the series are known:

		B.P. ° C.
Acetic anhydride	$(CH_3.CO)_2O$	138°
Propionic anhydride	$(C_2H_5.CO)_2O$	165°
Butyric anhydride	$(C_3H_7^{\alpha}.CO)_2O$	191°—193°
Isovaleric anhydride*	$(C_4H_9.CO)_2O$	215°
Trimethacetic anhydride	$[(CH_3)_3C.CO]_2O$	190°

(1759) ACETIC OXIDE OR ANHYDRIDE: $C_4H_6O_3 = (CH_3.CO)_2O$.—Acetic anhydride is most conveniently prepared by the action of acetic chloride on either acetic acid or sodic acetate. It is also formed on adding acetic chloride to baric oxide: the reaction commences in the cold, and is completed by heating the mixture in sealed tubes at 100° (212° F.). Calcic oxide is acted upon with such violence by acetic chloride that it becomes red-hot if much of the chloride be added at a time; plumbic oxide, however, is but slightly affected even at 150° (302° F.) (Gal, *Ann. Chem. Pharm.*, cxxviii. 126). According to Broughton (*Chem. Soc. Journ.*, xviii. 121), it may be obtained by heating a mixture of plumbic acetate and carbonic bisulphide in sealed tubes at 165° (329° F.), plumbic sulphide and carbonic anhydride being the accessory products.

Acetic anhydride is a colourless, mobile, pungent-smelling liquid, of the sp. gr. 1·073 at 20°·5 (68°·9 F.); it boils at 138° (280°·4 F.). When poured into water, it falls through it in oily drops, which however soon dissolve, forming acetic acid; alkaline solutions decompose it much more readily, and it is also acted upon by anhydrous basic oxides, such as calcic oxide, the corresponding metallic acetate being formed. A number of acid oxides also enter into reaction with it: thus with chlorine monoxide, it forms chlorine acetate—a compound which has already been described; and when it is boiled with arsenious and boric oxides, syrupy liquids are obtained, which solidify on cooling to vitreous masses: the compounds thus produced may be regarded as formed by the displacement of H in the COOH group of acetic acid by the oxygenated radicles AsO and BO. These compounds, however, unlike those produced by the agency of the basic oxides, are all readily decomposed by water.

Acetic anhydride is dissolved by ethylic alcohol with formation of ethylic acetate, and it enters into reaction more or less readily with all alcohols and hydroxy-compounds in a similar manner.

It is also readily acted upon by ammonia and by many amines, forming acid amides; for example:

$$\underset{\text{Acetic anhydride.}}{(CH_3.CO)_2O} + 2NH_3 = \underset{\text{Acetamide.}}{CH_3.CO(NH_2)} + \underset{\text{Ammonic acetate.}}{CH_3.COONH_4}.$$

On passing chlorine into acetic anhydride heated to 100° (212° F.), acetic chloride distils over, leaving monochloracetic acid in the retort: $(CH_3.CO)_2O + Cl_2 = CH_3.COCl + CH_2Cl.COOH$; bromine acts upon it in a similar manner even more readily, but iodine is without action even at 200° (392° F.). It is also readily decomposed by hydrochloric acid gas at 100° (212° F.), acetic chloride and acetic acid being produced: $(CH_3.CO)_2O + HCl = CH_3.COCl + CH_3.COOH$. Phosphoric pentachloride entirely converts it into acetic chloride: $PCl_5 + (CH_3.CO)_2O = 2CH_3.COCl + POCl_3$.

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* Probably a mixture of the anhydrides of isoprimary and secondary valeric acids.

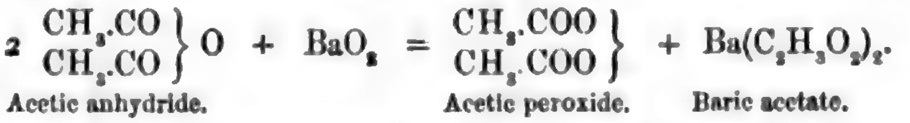
When a mixture of acetic anhydride and acetic acid is treated with sodium amalgam, the hydrogen liberated from the acid reduces the anhydride, converting it into ethylic alcohol. The mixed anhydrides furnish a mixture of the two corresponding alcohols, acetobutyric anhydride, for example, yielding ethylic and butylic alcohols (Linnemann, *Ann. Chem. Pharm.*, clxi. 185).

Zincic ethide acts with great violence on acetic anhydride, but if a mixture of ethylic iodide and acetic anhydride be dropped upon a quantity of zinc-sodium alloy, the reaction takes place more gradually, and is complete in about 30 hours; if water be then carefully added, and the mixture distilled, methylethylketone is obtained (M. Saytzeff, *Zeits. Chem.*, [2], vi. 104).

(1760) **Trimethacetic Anhydride**: $[C(CH_3)_3.CO]_2O$, obtained by heating a mixture of trimethacetic chloride and an excess of potassic trimethacetate in sealed tubes at 150° (302° F.), is a colourless liquid, lighter than water, possessing a faint, peculiar, but not pungent odour; it boils at about 190° (374° F.). Cold water has apparently no action upon it, and even dilute potassic hydrate solution attacks it but slightly, although it is violently acted upon by a slightly warm concentrated solution (Butlerow, *Ann. Chem. Pharm.*, clxxiii. 374).

(1761) **Acetic Thianhydride**: $(CH_3.CO)_2S$.—This compound may be prepared by gradually adding acetic chloride to well-cooled crystallized potassic sulphide. It is a colourless liquid, of alliaceous odour, boiling at 121° (249°·8 F.); it is not acted upon by dilute nitric acid, but the fuming acid dissolves it, forming acetic and sulphuric acids (Lukaschewicz, *Zeits. Chem.*, [2], iv. 642).

(1762) **Acetic Peroxide**: $(CH_3.COO)_2$.—This compound is formed by the action of baric peroxide on acetic anhydride, in accordance with the equation:



$$2\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O + BaO_2 = \left.\begin{matrix}CH_3.COO\\CH_3.COO\end{matrix}\right\} + Ba(C_2H_3O_2)_2.$$

Acetic anhydride. Acetic peroxide. Baric acetate.

In preparing it, the anhydride is dissolved in anhydrous ether, and the peroxide added very gradually, as the reaction is attended with development of heat; the solution is then filtered from the baric acetate, the ether carefully distilled off at as low a temperature as possible, and the residue washed with water until the washings are no longer acid.

Acetic peroxide is a viscid liquid, extremely pungent to the taste; it is highly unstable, and a most dangerous substance to manipulate, as it explodes with great violence when gently heated. Like all peroxides, it exhibits pronounced oxidizing properties, immediately decolorizing a solution of sulphindigotic acid, converting potassium ferrocyanide into ferricyanide, and liberating iodine from hydriodic acid and potassic iodide, but it does not reduce chromic or permanganic acid in an acid solution; on adding to it a solution of baric hydrate, baric acetate and hydrated baric peroxide are at once formed (Brodie, *Roy. Soc. Proc.*, ix. 361).

Butyric and *isovaleric peroxides* have been prepared in a similar manner, and appear to resemble the acetic compound in their properties (*ibid.*, xii. 655).

(1763) **Acetic Disulphide**: $(CH_3COS)_2$.—This compound apparently bears the same relation to thiacetic acid that acetic peroxide bears to acetic acid, and may be produced by the action of iodine on metallic salts of thiacetic acid (Kekulé and Linnemann): $2CH_3.COSK + I_2 = (CH_3.COS)_2 + 2KI$, or by electrolysis of these salts (Bunge, *Deut. chem. Ges. Ber.*, iii. 295, 911), *e.g.*: $2CH_3.COSK = (CH_3.COS)_2 + 2K$. It forms large colourless crystals, which melt at 20° (68° F.), and are readily soluble in alcohol, ether, and carbonic bisulphide, but insoluble in water; it is slowly decomposed by cold, and quickly by boiling water, sulphur and thiacetic acid being formed. It cannot be distilled.

(1764) HALOID DERIVATIVES OF THE ACIDS OF THE ACETIC SERIES.—These are formed from the unsubstituted acids by the displacement of one or more atoms of hydrogen in the C_nH_{2n+1} group by the corresponding number of atoms of chlorine, bromine or iodine. The chloro- and bromo-acids may be produced by a variety of methods which are more or less general.

1. By the direct action of chlorine or bromine on the acids themselves; thus:

$$CH_3.COOH + Br_2 = CH_2Br.COOH + HBr.$$

Acetic acid. Bromacetic acid.

2. By the action of these halogens on the anhydrides derived from the acids; *e.g.*:

$$(CH_3.CO)_2O + Cl_2 = CH_3.COCl + CH_2Cl.COOH;$$

Acetic anhydride. Acetic chloride. Chloracetic acid.

and also by their action on ethereal salts of the acids:

$$CH_3.COOC_2H_5 + Br_2 = CH_2Br.COOH + C_2H_5Br.$$

Ethylic acetate. Bromacetic acid.

Probably in this and the preceding case, simple haloid derivatives of the compound employed are first produced, but are at once acted upon by the haloid acid formed simultaneously:

$$(CH_3.CO)_2O + Br_2 = CH_2Br.CO.O.CO.CH_3 + HBr;$$
$$CH_2Br.CO.O.CO.CH_3 + HBr = CH_2Br.COOH + CH_3.COBr.$$

4. By the combination of the acids of the $C_nH_{2n-1}.COOH$ and $C_nH_{2n-3}.COOH$ series (*α*) with haloid acids, and (*β*) with halogens:

$$C_2H_3.COOH + HI = C_2H_4I.COOH.$$

Acrylic acid. Iodopropionic acid.

$$C_2H_3.COOH + Br_2 = C_2H_3Br_2.COOH.$$

Acrylic acid. Dibromopropionic acid.

5. By the action of haloid acids on acids of the lactic series:

$$CH_2(OH).CH_2.COOH + HI = CH_2I.CH_2.COOH + OH_2.$$

α-Hydroxypropionic acid. α-Iodopropionic acid.

6. By the action of the haloid phosphorus compounds on acids of the lactic series, the acid halide which is formed being subsequently decomposed by water:

$$CH_3.CH(OH).COOH + 2PCl_5 = CH_3.CHCl.COCl + 2POCl_3 + 2HCl;$$

β-Hydroxypropionic acid. β-Chloropropionic chloride.

$$CH_3.CHCl.COCl + OH_2 = CH_3.CHCl.COOH + HCl.$$

β-Chloropropionic chloride. β-Chloropropionic acid.

7. By oxidation of haloid derivatives of alcohols of the ethylic series:

$$\underset{\text{Dibromopropylic alcohol.}}{CH_2Br.CHBr.CH_2.OH} + 2(O + OH_2) = \underset{\text{Dibromopropionic acid.}}{CH_2Br.CHBr.COOH} + 2OH_2.$$

8. By oxidation of haloid derivatives of aldehydes of the $C_nH_{2n+1}.COH$ series:

$$\underset{\text{Trichlorethaldehyde.}}{CCl_3.COH} + (O + OH_2) = \underset{\text{Trichloracetic acid.}}{CCl_3.COOH} + OH_2.$$

In their general properties they most closely resemble the parent acids, although they are less stable compounds; in addition, however, to what may be termed the ordinary reactions of acids, many of them—especially the monohaloid acids—enter readily into reactions of double decomposition, exchanging the halogen for other radicles. For example, when heated with water or the weaker basic hydrates, they are converted into hydroxy-acids, the group OH displacing the halogen:

$$\underset{\text{Chloracetic acid.}}{CH_2Cl.COOH} + OH_2 = \underset{\text{Hydroxyacetic (glycolic) acid.}}{CH_2(OH).COOH} + HCl;$$

in a similar manner, by the action of ammonia, they are converted into amido-acids:

$$\underset{\text{Chloracetic acid.}}{CH_2Cl.COOH} + 3NH_3 = \underset{\text{Ammonic amidacetate.}}{CH_2(NH_2).COONH_4} + NH_4Cl.$$

Many of them, especially those derived from the higher homologues of acetic acid and those containing several atoms of halogen, lose the elements of one or more molecules of haloid acid when distilled alone, or heated with an alkali, and are converted into acids, or haloid derivatives of acids, isologous with the acids of the acetic series.

Haloid derivatives of formic acid are unknown, this acid being completely decomposed by chlorine and bromine, but ethereal salts of chloroformic acid, Cl.COOH, and of cyanoformic acid are obtainable (1788).

(1765) CHLORACETIC ACIDS.—Acetic acid, even if heated to the boiling point, is but slowly acted upon by chlorine in the dark or in diffused light; it is more rapidly acted upon in bright sunshine, and ultimately converted into trichloracetic acid. The chlorination is much more readily effected if iodine chloride be employed; and according to H. Müller (*Journ. Chem. Soc.*, xvii. 398), the mono- and dichlorinated acid may even be advantageously prepared by passing chlorine into the boiling acid to which a small quantity of iodine has been added (about 50 grams to the ½ litre); the two acids are separated and purified by fractional distillation. Chloracetic acid is most readily obtained, however, by passing chlorine into acetic anhydride heated to 100° (212° F.); acetic chloride then distils over, leaving the almost pure acid in the retort (Gal). Pure dichloracetic acid is best prepared from trichlorethaldehydrol (chloral-hydrate), by converting this compound into ethylic dichloracetate by the action of potassic cyanide in presence of alcohol; thus: $CCl_3.CH(OH)_2 + C_2H_5.OH + KCN = CHCl_2.COOC_2H_5 + KCl + HCN + OH_2$. A quantity of the pure cyanide slightly in excess of that indicated by this equation is placed in a flask connected with a reversed condenser (provided with a tube for the escape of the hydrocyanic acid gas) and covered with a layer of absolute alcohol; a moderately concentrated alcoholic solution of trichlorethaldehydrol is then added drop by drop, as the action is violent. The product is mixed with water, and the oil which separates is then washed with water and afterwards with a very dilute solution of sodic hydrate, distilled in a current of steam, dried and rectified. The pure ethylic salt thus obtained is diluted with about an equal volume of alcohol and mixed with an alcoholic solution of the requisite amount of pure potassic hydrate; decomposition at once takes place, and the liquid becomes filled with a mass of crystals of potassic dichloracetate. These crystals are dried and introduced into a combustion tube, placed in an inclined furnace and connected at the one end with an apparatus for evolving hydrochloric acid gas and at the other with a condenser; on passing the gas, it is absorbed and dichloracetic acid is produced. When the gas escapes from the condenser, the decomposition may be judged complete, and the acid is distilled off in a slow stream of hydrochloric acid (Wallach, *Ann. Chem. Pharm.*, clxxiii. 288; *Deut. chem. Ges. Ber.*, ix. 1212).*

Trichloracetic acid is readily obtained by adding trichlorethaldehydrol (chloral-hydrate) to about three times its weight of fuming nitric acid, completing the reaction by warming, and then distilling.

The chloracetic acids, and, indeed, all the haloid derivatives of acetic acid, are highly caustic substances, causing painful blisters if applied to the skin; they are readily soluble in water, and are reconverted into acetic acid by nascent hydrogen.

Chloracetic acid forms rhombic plates, melting at 62° (143°·6 F.), and boils undecomposed at about 186° (366°·8 F.); it furnishes a number of crystalline metallic salts, amongst others the silver salt $CH_2Cl.COOAg$, which separates from a hot aqueous solution on cooling in colourless nacreous scales. By boiling with water, chloracetic acid is converted into hydroxyacetic acid (glycolic acid), $CH_2(OH).COOH$.

Dichloracetic acid is liquid at ordinary temperatures, but solidifies when cooled below 0° (32° F.); it boils at about 190° (374° F.). Its potassic salt crystallizes in glistening plates.

Trichloracetic acid crystallizes in colourless rhombohedra, melting at 52°·4 (126°·3 F.); it boils at about 195° (383° F.). It furnishes a series of metallic salts, which may be obtained, many of them in the crystalline state, by neutralizing a solution of the acid with the corresponding metallic oxide or hydrate, and then concentrating over sulphuric acid (comp. Clermont, *Ann. Chim. Phys.*, [5], ii. 401; Judson, *Deut. chem. Ges. Ber.*, iii. 782); if the solution be heated, the trichloracetate is decomposed, the corresponding formate and trichloromethane being produced.

The *ethylic* salts of these acids boil respectively at 143° (289°·4 F.), 156° (312°·8 F.), and 164° (327°·2 F.).

Monochloracetic chloride, $CH_2Cl.COCl$, boils at 105° (221° F.) and *trichloracetic chloride*, $CCl_3.COCl$, at 118° (244°·4 F.).

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* The manner in which this remarkable reaction is to be interpreted has been the subject of much discussion (comp. Wallach, *ibid.*, x. 2120; Claus, *ibid.*, xi. 498).

(1766) **Bromacetic Acids.**—*Monobromacetic acid:* $CH_2Br.COOH$, may be formed by the direct action of bromine on acetic acid; by heating ethylic acetate with bromine at 150° (302° F.) (Crafts); by heating hydroxyacetic (glycolic) acid with a saturated solution of hydrobromic acid at 100° (212° F.) (Kekulé); by the action of bromine on anhydrous glycerol (Barth); and by oxidation of monobromacetylene in moist air (Glöckner, *Ann. Chem. Pharm., Sup.*, vii. 114). To prepare it, a mixture of bromine with twice the requisite amount of acetic acid is enclosed in strong tubes, the temperature of which is then merely raised to 150° (302° F.);* when sufficiently cool, the tubes are carefully opened and their contents heated in a retort to 200° (392° F.); the residue consists of a mixture of the monobromo-acid with a small quantity of dibromacetic acid, and may be purified by conversion into the lead salt, &c. (Perkin and Duppa, *Journ. Chem. Soc.*, xi. 22).

Dibromacetic acid: $CHBr_2.COOH$, may be obtained by the action of bromine in bright sunshine on heated bromacetic acid (*ibid.*, xii. 1), but, according to Carius, it is best prepared by heating a mixture of ethylic acetate and a slight excess of bromine in sealed tubes at 120°—130° (248°—266° F.) (*Deut. chem. Ges. Ber.*, iii. 336).

Tribromacetic acid: $CBr_3.COOH$, is formed by the action of water on tribromacetic bromide.

Bromacetic acid forms deliquescent rhombohedral crystals, melting below 100° (212° F.): it boils at about 208° (406°·4 F.). Dibromacetic acid is also crystalline when pure; it boils between 225° and 230° (437°—446° F.), but is partially decomposed. Tribomacetic acid melts at 135° (275° F.), and boils at 250° (482° F.) (Gal): when heated with alkalies, it yields tribromomethane and a formate. Mono- and dibromacetic acids furnish a number of characteristic salts; the tribromacetates have not been examined.

The *bromacetic bromides* have been prepared by heating acetic bromide with bromine. A remarkable method of forming mono- and dibromacetic bromides has also been recently described by Demole (*Deut. chem. Ges. Ber.*, xi. 315, 1302), consisting in agitating α-dibromethylene, $CHBr{=}CHBr$, and tribromethylene respectively with dry oxygen, which is rapidly absorbed with considerable development of heat. It may be supposed that the corresponding oxide is first formed, but is immediately converted into the acid bromide by an isomeric change perhaps similar to that by which ketones of the form $C_nH_{2n+1}.CO.C(C_nH_{2n+1})_3$ are produced from the glycols of the form $[C(C_nH_{2n+1})_2.OH]_2$ (comp. p. 773). α-Chlorobromethylene, $CHCl{=}CHBr$, yields a mixture of bromacetic chloride and chloracetic bromide, but monobrom-, tetrachlor- and tetrabromethylene are not altered on agitation with oxygen. The formation of trichloracetic acid on exposure of tetrachlorethylene in contact with water and chlorine to sunshine (Kolbe), and of trichloracetic chloride by the action of sulphuric anhydride on the same body (Prudhomme), may doubtless be classed in the same category of reactions.

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* Hell and Müllhäuser have recently shown (*Deut. chem. Ges. Ber.*, x. 2102; xi. 241) that when a mixture of acetic acid, bromine and carbonic bisulphide is allowed to stand, prismatic crystals of a compound of the formula $C_2H_4O_2Br_2$ are deposited, which are not formed in the absence of the bisulphide. On adding the bisulphide to the mixture of bromine and acetic acid heat is developed, and if sufficient be added crystals soon separate, the rate at which crystals form being apparently strictly proportional to the amount of bisulphide present; moreover, carbonic bisulphide not only induces the formation of acetic dibromide, but also greatly facilitates the formation of substitution derivatives. Although apparently no change takes place on heating a mixture of bromine and acetic acid at 100° (212° F.) for about 40 hours, after about 45 hours crystals are formed, but these are perhaps a compound of acetic acid, bromine and hydrobromic acid. By adding bromine to a saturated solution of hydrobromic acid in acetic acid crystalline compounds of the formula $2C_2H_4O_2.Br_2.HBr$ or $4C_2H_4O_2.3Br_2.2HBr$ are formed according to the proportion of bromine used. In a similar manner a crystalline compound of bromine with acetic and hydrochloric acids may be obtained, and crystalline substances are also produced sooner or later on adding iodine, sulphur, phosphorus or ethyl bromide to a mixture of bromine and acetic acid. Formic acid apparently also forms an additive compound with bromine.

(1767) IODACETIC ACIDS.—*Mono-* and *diiodacetic* acids have been obtained by displacing the bromine in the ethylic salts of the corresponding bromo-acids by iodine by double decomposition with potassic iodide, converting the ethylic salts thus prepared into baric salts by treatment with baric hydrate solution, and displacing the metal in these latter by hydrogen by means of a mineral acid.

They are both crystalline, and furnish crystalline salts (Perkin and Duppa, *Phil. Mag.* [4], xviii. 54; *Journ. Chem. Soc.*, xiii. 1). Moniodacetic acid is reduced to acetic acid by a concentrated solution of hydriodic acid even in the cold (Kekulé).

(1768) CYANACETIC ACID: $CH_2(CN).COOH$.—This acid is prepared by heating ethylic monochloracetate with an aqueous solution of potassic cyanide. It is a crystalline substance melting at 80° (176° F.). When heated to 165° (329° F.) it is resolved into carbonic anhydride and cyanomethane, $CH_3.CN$ (Van t'Hoff). Its ethylic salt boils at about 207° (404°·6 F.).

(1769) HALOID DERIVATIVES OF PROPIONIC ACID.—The action of halogens on propionic acid has been but little studied, most of its haloid derivatives having been obtained by indirect methods. The mono-derivatives exist in the two isomeric modifications represented respectively by the formulæ $CH_2X.CH_2.COOH$ and $CH_3.CHX.COOH$, and of the three possible dichloro- and dibromo-acids those of the forms $CH_2X.CHX.COOH$ and $CH_3.CX_2.COOH$ are known, but the higher derivatives have not been examined.*

α-Monochloro-, bromo-, and iodopropionic acids are formed by the direct union of the corresponding haloid acids with acrylic acid, thus: $CH_2{=}CH.COOH + HCl = CH_2Cl.CH_2.COOH$. The iodo-acid (usually termed β-iodopropionic acid) may also be produced by the action of hydriodic acid or phosphorus iodide on glyceric acid: $CH_2(OH).CH(OH).COOH + 2HI = CH_2I.CHI.COOH + 2OH_2$; $CH_2I.CHI.COOH + HI = CH_2I.CH_2.COOH + I_2$; and by treatment with chlorine or bromine, the acid thus prepared may be converted into the corresponding chloro- or bromo-acid. They are all crystalline. The iodo-acid forms large colourless plates difficultly soluble in cold water, melting at 83°—84° (181°·4—183°·2 F.). The bromo-acid melts at 61°·5 (142°·7 F.); the chloro-acid at 40°·5 (104°·9 F.).

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* Until recently it has been the custom to employ the letters α, β, &c., merely to distinguish isomerides and without reference to their constitution, the compound first discovered usually being designated as the α-body, and that next in order of discovery as the β-compound, but of late these letters have been used with some slight regard to system, the mono-derivatives of normal primary acids of the form $C_nH_{2n+1}.CHX.COOH$ being as a rule termed α-compounds. It appears more desirable, however, to term those of the form $CH_2X.(CH_2)_n.COOH$ α-derivatives, as they belong to the same class of di-derivatives of the normal paraffins as the α-di-haloid derivatives such as the dibromethane $CH_2Br.CH_2Br$ and the dibromopropane $CH_2Br.CH_2.CH_2Br$. The constitution of other deriva-

β-Chloropropionic acid, which doubtless would be the first product of the action of chlorine on propionic acid, has been obtained by acting on ordinary fermentation lactic acid, $CH_3.CH(OH).COOH$, with phosphoric pentachloride and treating the resulting chloropropionic chloride with water. The *β-bromo*-acid may be formed by heating propionic acid with bromine at 150° (302° F.), or fermentation lactic acid with a saturated solution of hydrobromic acid. *β-Iodopropionic* acid is produced in a similar manner by the action of phosphorus iodide on lactic acid (Wichelhaus). These compounds are all liquid.

Of the two sets of isomerides, the α-acids are relatively much more stable bodies, and enter less readily into reactions of double decomposition.

Little is known of *αβ-dichloropropionic* acid. The β^2-acid, $CH_3.CCl_2COOH$ has been carefully examined, however (Otto and Beckurts, *Deut. chem. Ges. Ber.*, ix. 1876; x. 2037); it is obtained by heating dichlorocyanethane, $CH_3.CCl_2.CN$ (formed by chlorinating propionitrile) with concentrated hydrochloric acid or slightly diluted sulphuric acid, and its ethylic salt may be produced by distilling pyruvic acid with phosphoric pentachloride and treating the resulting acid chloride with alcohol. This acid furnishes crystalline salts, which are readily decomposed on heating their aqueous solutions, a metallic chloride and the chloracrylic acid $CH_2{=}CCl.COOH$, being formed, although the acid itself is not appreciably altered by boiling water. By the action of zinc and sulphuric acid at ordinary temperatures it is readily converted into propionic acid. It is not acted upon by chlorine even in presence of iodine at an elevated temperature. It is crystalline at low temperatures, and boils at about 190° (374° F.).

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tives is conveniently indicated by assigning the letter α to the terminal CH_3 group and the letters β, γ, &c. to the several CH_2 groups in the formula commencing with that next to the terminal CH_3 group. The application of this system will be best understood from the following examples:

α β	
$CH_3.CH_2.COOH$	Propionic acid.
$CH_2Br.CH_2.COOH$	α-Bromopropionic acid.
$CH_3.CHBr.COOH$	β- ,, ,,
$CHBr_2.CH_2.COOH$	α²-Dibromopropionic acid.
$CH_2Br.CHBr.COOH$	α-β- ,, ,,
$CH_3.CBr_2.COOH$	β²- ,, ,,
$CBr_3.CH_2.COOH$	α³-Tribromopropionic ,,
$CHBr_2.CHBr.COOH$	α²-β- ,, ,,
$CH_2Br.CBr_2.COOH$	α-β²- ,, ,,
$CBr_3.CHBr.COOH$	α³-β-Tetrabromopropionic acid.
$CHBr_2.CBr_2.COOH$	α²-β²- ,, ,,

But in the case of the higher acids, and especially of derivatives of acids other than normal primary acids, it will in most cases be desirable to employ names indicating the relation to lower terms of the series: thus, the two bromobutyric acids

$$CH_3.CH_2.CHBr.COOH$$
$$CH_3.CBr(CH_3).COOH$$

are most conveniently distinguished by terming them respectively ethylbromacetic acid and dimethylbromacetic acid; while of the two isomeric acids

$$CH_3.CHBr.CH_2.COOH$$
$$CH_2Br.CH(CH_3).COOH$$

the former may be designated α-methyl-α-bromopropionic acid, and the latter β-methyl-α-bromopropionic acid.

αβ-Dibromopropionic acid is formed by combining acrylic acid with bromine; by oxidation of the dibromopropylic alcohol prepared by combining allylic alcohol with bromine; and by the combination of both α- and β-bromacrylic acid with hydrobromic acid. *β^2-Dibromopropionic* acid is obtained by the action of bromine on propionic acid at 200°—220° (392°—428° F.) (Münder, Caspary, Philippi, Wagner and Tollens, *Ann. Chem. Pharm.*, cxlvii. 222, 240; clxxi. 314, 340). Both acids furnish crystalline salts, which—like those of the dichloro-acid—are decomposed by heat, the salts of the β^2-acid, with the exception of the silver salt, being, however, the more stable. On treatment with an alcoholic solution of potassic hydroxide, they are converted into the isomeric bromacrylic acids, $CHBr{=}CH.COOH$ and $CH_2{=}CBr.COOH$ respectively; and they are further distinguished by their behaviour with zinc and sulphuric acid, whereby the αβ-acid is reduced to acrylic acid, whilst the β^2-acid is converted into propionic acid. The αβ-acid melts at about 65° (149° F.), the β^2-acid at 61° (141°·8 F.).

(1770) HALOID DERIVATIVES OF HIGHER ACIDS.—We are almost unacquainted with the haloid derivatives of acids higher in the series than propionic acid, for although haloid derivatives of several have been obtained, very few have as yet been prepared in a state of purity. As compared with acetic acid, the higher acids are apparently more readily acted upon by the halogens; bromine, for instance, gradually converting normal butyric and caproic acids into bromo-acids, even at a temperature of 100° (212° F.). The normal primary acids, like the normal paraffins, appear to furnish isomeric mono-derivatives in proportions which vary with the temperature at which the reaction takes place; thus, according to Erlenmeyer (*Deut. chem. Ges. Ber.*, x. 636), when normal butyric and caproic acids are digested with bromine at 100 (212° F.), mono-bromo-acids of the form $C_nH_{2n+1}CHX.COOH$ are almost exclusively produced, whereas when the action is effected by heating to 140° (284° F.) the product contains a much larger proportion of an isomeric bromo-acid (comp. Popoff, *ibid.*, viii. 540). Isoprimary valeric acid is converted into the bromo-acid of the formula $(CH_3)_2CH.CHBr.COOH$, whilst the secondary acid, dimethacetic (isobutyric) acid, furnishes dimethbromacetic acid, $CBr(CH_3)_2.COOH$. Hence it would appear that when acids of the form $R.CH_2.COOH$ and $R_2.CH.COOH$ are submitted to the action of bromine, the chief tendency, in the first instance, is for hydrogen associated with the carbon atom with which the carboxyl is united to be displaced.

Butyric acid derivatives.—According to Markownikoff (*Zeits. Chem.*, 1868, 621), normal butyric acid is with difficulty attacked by chlorine even at its boiling point; the action takes place much more readily if a little iodine be added, and together with higher chlorinated derivatives, a crystallizable chlorobutyric acid melting at 98° (208°·4 F.) is produced in small quantity. The same chemist states (*Ann. Chem. Pharm.*, cliii. 240) that by submitting boiling butyric chloride to the action of chlorine in presence of iodine, a chlorobutyric chloride, boiling at about 130° (266° F.), is obtained, the acid prepared from which does not crystallize, and which has the formula $CH_3.CH_2.CHCl.COOH$, as it is convertible into the hydroxy-acid $CH_3.CH_2.CH(OH).COOH$. Balbiano, however (*Gaz. chim. Ital.*, viii. 90), has recently prepared a chloro-acid by the action of chlorine in sunlight on butyric acid heated to about 95° (203° F.), to which he assigns the formula $CH_3.CHCl.CH_2.COOH$ as it furnishes a small amount of the hydroxy-acid $CH_3.CH(OH).CH_2.COOH$, together with a considerable amount of crystalline crotonic acid on treatment with baric hydroxide solution; it is far more probable, however, that his product chiefly consisted of the acid $CH_3.CH_2.CHCl.COOH$, mixed with a small proportion of the isomeric acid corresponding to the hydroxy-acid obtained, since it would appear that the haloid derivatives of the form $C_nH_{2n+1}.CHX.COOH$ are the most readily convertible into acids of the acrylic series.

By oxidizing trichlorotetraldehydrol (1632)—so-called croton-chloral hydrate—with nitric acid, a crystalline trichlorobutyric acid, $C_3H_4Cl_3.COOH$, is produced, which melts at 44° (111°·2 F.) (comp. *Ann. Chem. Pharm.*, clxxxii. 181). The oxidation takes place with less facility than that of trichlorethaldehydrol. This acid furnishes a number of crystalline metallic salts, which, however, are less characteristic than the trichloracetates; its ethylic salt boils at 212° (413°·6 F.). It is with difficulty acted upon by phosphoric pentachloride, and converted into the acid chloride, which boils at about 164° (327°·2 F.) (Judson, *Deut. chem. Ges. Ber.*, iii. 785). The chlorocrotonic acid, $C_3H_4Cl.COOH$, obtained by reduction of this acid, combines with bromine, forming a crystalline *dibromochlorobutyric acid*, $C_3H_4ClBr_2.COOH$, which melts at 92° (197°·6 F.) (Sarnow).

The mono-bromobutyric acids formed by the action of bromine on normal butyric acid have not yet been prepared in a pure state (comp. Hell, *ibid.*, vi. 28; vii. 560). A similar mixture to that obtained from butyric acid and bromine is apparently formed by the combination of crystalline crotonic acid, $CH_3.CH{=}CH.COOH$, with hydrobromic acid (Hemilian; Alberti, *ibid.*, ix. 1194). Both products furnish crystalline crotonic acid on decomposition with alkalies, or even boiling water.

According to Schneider and Friedel and Machuca (*Ann. Chem. Pharm.*, cxx. 281; *Suppl.* 2, 70), butyric acid furnishes an oily dibromo-derivative when heated with the necessary amount of bromine at 130°—150° (266°—302° F.). This acid is said to furnish a brombydroxybutyric acid on digestion with baric hydroxide solution, which is convertible into dihydroxybutyric acid by the action of argentic hydroxide (Petrieff and Eghis, *Deut. chem. Ges. Ber.*, viii. 265); if this be the case, it is probable that the bromine atoms are associated with different carbon atoms.

According to Hemilian and Alberti (*loc. cit.*), crystalline crotonic acid readily combines with hydriodic acid, forming a crystalline *iodobutyric* acid of the formula $CH_3.CH_2.CHI.COOH$, which melts at 110° (230° F.): a liquid isomeride is formed at the same time.

By heating dimethacetic or isobutyric acid with bromine at 140° (284° F.), it is converted into dimethbromacetic acid, $CBr(CH_3)_2.COOH$, which separates from ether in large crystalline plates melting at 48° (118°·4 F.); it distils with slight decomposition at 199° (390°·2 F.). Its ethylic salt boils at 160° (320° F.). By boiling water it is converted into dimethhydroxyacetic acid, $C(OH)(CH_3)_2.COOH$, an alcoholic solution of potassic hydroxide converting it into the corresponding dimethethoxyacetic acid, $C(OC_2H_5)(CH_3)_2.COOH$ (Markownikoff; Hell and Waldbauer, *ibid.*, x. 448).

The corresponding *dimethiodacetic* acid, $CI(CH_3)_2.COOH$, is formed by combining methacrylic acid with hydriodic acid; it melts at 37° (98°·6 F.).

§ II. AMIDO- AND HYDROXY-ACIDS DERIVED FROM THE ACIDS OF THE ACETIC SERIES.

(1771) AMIDO-ACIDS OR GLYCINES.—These compounds are formed by the introduction of the monad radicle NH_2 (amidogen) in place of a single atom of hydrogen in the C_nH_{2n+1} group of the acids of the acetic series. Compounds formed by the introduction of a greater number of NH_2 groups have not yet been obtained. A number of them are products of the action of hydrating agents on various albumenoid substances; they may be prepared synthetically by either of the following methods.

1. By digesting the mono-haloid derivatives of the acids of the acetic series with an aqueous or alcoholic solution of ammonia; thus:

$$C_nH_{2n}X.COOH + 3NH_3 = C_nH_{2n}(NH_2).COONH_4 + NH_4X.$$

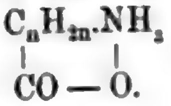
$$\underset{\text{Iodopropionic acid.}}{C_2H_4I.COOH} + 3NH_3 = \underset{\text{Ammonic amidopropionate.}}{C_2H_4(NH_2).COONH_4} + NH_4I.$$

More complex compounds formed by the action of two and three molecules of the acid on a single molecule of ammonia are frequently produced simultaneously (comp. 1773).

2. By acting on the amido-alcohols formed by the union of the aldehydes of the $C_nH_{2n+1}.COH$ series with ammonia (p. 720) with hydrocyanic acid, and digesting the product with hydrochloric acid solution. The amount of amido-acid produced in this manner is not equivalent to that of the aldehyde employed, but always less, and varies according to the conditions of experiment; apparently the amido-cyanide resulting from the action of the hydrocyanic acid [$C_nH_{2n+1}.CH(NH_2).OH + HCN = C_nH_{2n+1}.CH(NH_2).CN + OH_2$] undergoes condensation, and the amido-acid finally obtained is chiefly derived from the product or products of condensation, and not directly formed from the amido-cyanide by the simple conversion of the group CN into COOH.

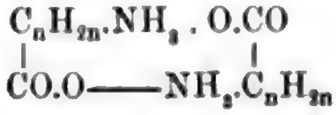
Properties.—The glycines are crystalline substances more or less soluble in water. They either possess a sweet taste or are tasteless, and are without action on vegetable colouring matters. They not only enter into reaction with metallic oxides, hydrates, and carbonates to form metallic salts, but also combine directly with acids and with many metallic salts; and their alkaline solutions dissolve cupric hydrate. Judging from the behaviour of glycine and leucine, their aqueous solutions are coloured blood-red by ferric chloride and intense blue by cupric sulphate; they reduce a solution of mercurous nitrate slowly in the cold, but more rapidly on heating; and they are not precipitated from neutral solutions by mercuric salts alone, but are thrown down if sodic carbonate be added simultaneously (Hofmeister, *Ann. Chem. Pharm.*, clxxxix. 6). They are not decomposed by boiling with aqueous solutions of alkaline hydrates. Nitrous acid converts them into the corresponding acids of the lactic series.

Inasmuch as the glycines are destitute of acid taste, and have no action on vegetable colours, and may even be crystallized from alcohol in presence of ammonia, it can hardly be doubted that they no longer contain the group COOH: in other words, although derived from haloid compounds of the form $C_nH_{2n}X.COOH$, they cannot be represented as constituted on the same type, according to the formula $C_nH_{2n}(NH_2).COOH$. Their properties are accounted for, however, on the assumption that they are compounds of the formula



$$\begin{array}{l} C_nH_{2n}.NH_2 \\ \;| \qquad\quad | \\ CO - O. \end{array}$$

But their high melting points, the composition of certain of their compounds with acids, and the circumstance that they are capable of uniting together (Hofmeister), render it far more probable that their molecular weights are at least double as great as this formula would indicate; on this hypothesis they may be represented by the formula



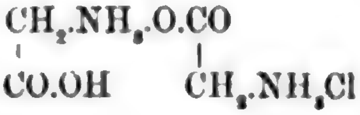
$$\begin{array}{l} C_nH_{2n}.NH_2\,.\,O.CO \\ \;| \qquad\qquad\qquad | \\ CO.O —— NH_2.C_nH_{2n} \end{array}$$

Confirmation of this view of the constitution of the glycines is afforded by the fact that hippuric or benzamidacetic acid, $CH_2(NH.COC_6H_5)COOH$, exhibits a marked acid reaction with vegetable colours, the introduction of the negative radicle $CO.C_6H_5$ in place of one of the hydrogen atoms in the NH_2 group having neutralized the tendency of the nitrogen to pass to the pentad condition.

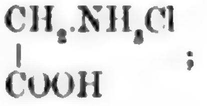
The glycines at present known have all been prepared from haloid derivatives of acids of the acetic series in which the halogen is associated with the same carbon atom as the COOH group, or with a contiguous carbon atom. It may therefore be questioned whether the compounds derived from acids in which the halogen is associated with a carbon atom not contiguous to that united with the COOH group would be glycines or true amido-acids; it appears probable that the former would be the case if, as above suggested, the molecule of the glycines be derived from two molecules of the generating acid.

(1772) **Glycine**;* *Glycocine, Glycocoll or Amidacetic Acid:* [?] $C_2H_5NO_2$ or $C_4H_{10}N_2O_4$.—Glycine is formed by the action of hydrating agents on a variety of substances of animal origin, such as gelatin, hippuric acid and glycocholic acid, being most conveniently prepared by heating hippuric acid with concentrated hydrochloric acid, or gelatin with a solution of baric hydrate. It is produced on passing cyanogen gas into a boiling concentrated solution of hydriodic acid (Emmerling, *Deut. chem. Ges. Ber.*, vi. 1351): $NC.CN + 6HI + 2OH_2 = CH_2(NH_2I).COOH + 2I_2 + NH_4I$; by the action of nascent hydrogen on ethylic cyanoformate (cyanocarbonate), $CN.COOC_2H_5$ (Wallach, *Ann. Chem. Pharm.*, clxxxiv. 13); and together with so-called di- and triglycolamidic acids on boiling chloracetic acid with an aqueous solution of ammonia.

Glycine crystallizes from water in hard transparent monoclinic prisms, having a sweetish taste; it dissolves in about 4 parts of cold water, but is only sparingly soluble in alcohol. It melts at about 170° (338° F.), and decomposes at a slightly higher temperature. The metallic amidacetates formed by the action of the metallic carbonates, hydroxides or oxides on glycine, are mostly easily soluble; the most characteristic is the copper salt $C_4H_8N_2O_4Cu + OH_2$, which crystallizes from hot solutions in magnificent blue needles. Glycine forms two compounds with hydrochloric acid, which may be represented by the following formulæ:



$$\begin{array}{l} CH_2.NH_2.O.CO \\ \;| \qquad\qquad\;\; | \\ CO.OH \quad CH_2.NH_2Cl \end{array}$$



$$\begin{array}{l} CH_2.NH_2Cl \\ \;| \\ COOH \end{array} ;$$

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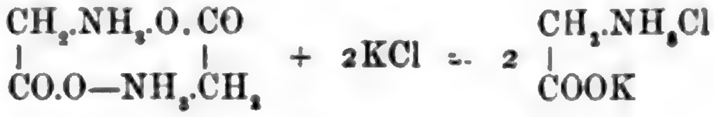
[*] Formoglycine is not known, but metallic and ethereal salts derived from it are readily obtained (comp. 1790).

and it also combines with a number of salts, such as the chlorides of potassium and sodium, forming well crystallized compounds, the probable nature of which is illustrated by the equation:



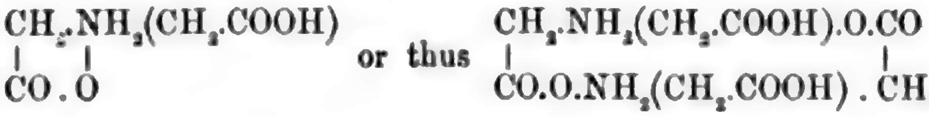
$$\begin{array}{l} CH_2.NH_2.O.CO \\ |\qquad\qquad\quad | \\ CO.O-NH_2.CH_2 \end{array} + 2KCl = 2\begin{array}{l} CH_2.NH_2Cl \\ | \\ COOK \end{array}$$

According to Hofmeister (*Ann. Chem. Pharm.*, clxxxix. 34), a solution of pure cupric amidacetate does not furnish a precipitate on the addition of sodic hydrate, and on adding a cupric salt to an alkaline solution of glycine, no precipitate is produced until the copper is in excess of the proportion $C_4H_{10}N_2O_4 : Cu$; doubtless therefore a definite compound is formed, such perhaps as is represented by the formula:

$$Cu\left\{\begin{array}{l} O.NH_2.CH_2.COONa \\ O.NH_2.CH_2.COONa \end{array}\right.$$

By heating an alcoholic solution of glycine with ethylic iodide, ethylic amidacetate hydriodide is produced, $CH_2(NH_3I).COOC_2H_5$; on treatment with argentic hydroxide, this yields ethylic amidacetate which decomposes on evaporation of the aqueous solution (comp. Betains).

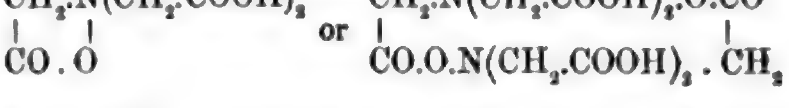
(1773) DI- AND TRIGLYCOLAMIDIC ACIDS.—As above stated, these compounds are formed together with glycine on boiling chloracetic acid with an aqueous solution of ammonia (for details of preparation, see Heintz, *ibid.*, cxlv. 49). *Diglycolamidic acid* crystallizes in large rhombic prisms, somewhat less soluble in water than glycine; it has a strong acid taste, and is capable of exchanging two atoms of hydrogen for metals, but exhibits a marked tendency to form mono-metallic salts, and probably therefore contains only a single COOH group, so that its formula may be written as follows:



$$\begin{array}{l} CH_2.NH_2(CH_2.COOH) \\ |\quad\ | \\ CO.O \end{array} \quad \text{or thus} \quad \begin{array}{l} CH_2.NH_2(CH_2.COOH).O.CO \\ |\qquad\qquad\qquad\qquad\qquad\ | \\ CO.O.NH_2(CH_2.COOH).CH_2 \end{array}$$

It also forms crystalline compounds with acids, such as the hydrochloride $NH_2Cl(CH_2.COOH)_2$. When submitted to the action of nitrous acid, it yields nitrosodiglycolamidic acid, $N(NO)(CH_2.COOH)_2$.

Triglycolamidic acid crystallizes in small hard prisms, which dissolve with difficulty in water, furnishing a strongly acid solution; when treated with baric carbonate, it exchanges only two atoms of hydrogen for metal, but forms trimetallic salts with less positive metals, so that its formula is probably either



$$\begin{array}{l} CH_2.N(CH_2.COOH)_2 \\ |\quad\ | \\ CO.O \end{array} \quad \text{or} \quad \begin{array}{l} CH_2.N(CH_2.COOH)_2.O.CO \\ |\qquad\qquad\qquad\qquad\quad\ | \\ CO.O.N(CH_2.COOH)_2.CH_2 \end{array}$$

It does not form stable compounds with acids, although it is more soluble in acids than in water. Nitrous acid is entirely without action upon it (Heintz, *ibid.*, cxxii. 257; cxxiv. 297; cxxxvi. 213; cxxxviii. 300).

(1774) HIPPURIC OR BENZAMIDACETIC ACID AND ALLIED COMPOUNDS; *Hippuric acid*: $C_9H_9NO_3 = CH_2.NH(COC_6H_5)COOH$.—Salts of this acid are normal constituents of human urine, although present in very small quantity (·03—·04 per cent. of acid), but often occur in large quantity in the urine of herbivora; the calcic salt may be directly crystallized out from concentrated horses' urine, and the acid may easily be prepared from horses' or cows' urine by evaporating the urine to about one-fourth its volume, and then acidulating it with hydrochloric acid: the crude acid which separates is dissolved in a dilute solution of sodic hydrate and sufficient sodic hypochlorite added to the boiling liquid to render it colourless, after which the acid is again precipitated by hydrochloric acid, and once recrystallized from boiling water. It may be artificially obtained by heating glycine with benzoic acid, or benzoic chloride, $C_6H_5.COCl$, with the silver or zinc salt of amidacetic acid, and is also formed in small quantity on heating chloracetic acid with benzamide, $C_6H_5.CO.NH_2$.

Hippuric acid crystallizes in colourless rhombic prisms, melting at 187°·5 (369° F.), which dissolve in about 600 pts. cold water, forming a strongly acid solution. It furnishes a number of metallic salts of the general formula $C_9H_8MNO_3$, but does not combine with acids; this, together with the fact that it has a marked acid reaction, indicates, as already pointed out, that it is a true amido-acid and not a glycine. By the action of chlorinating and brominating agents, a number of chlorinated and brominated hippuric acids have been formed; and when treated with concentrated nitric acid, it yields meta-nitrohippuric acid, convertible by reduction into amidohippuric acid, from which latter, by Griess's method, hydroxyhippuric acid may be formed (comp. Conrad, *Jour. pr. Chem.* [2], xv. 241). All these compounds result apparently from the displacement of hydrogen atoms in the C_6H_5 group. By the action of hydrating agents, and especially of boiling hydrochloric acid, hippuric acid is readily decomposed in the manner represented by the equation:

$$\underset{\text{Hippuric acid.}}{CH_2.NH(C_6H_5.CO).COOH} + OH_2 + HCl = \underset{\text{Amidacetic hydrochloride.}}{CH_2.NH_3Cl.COOH} + \underset{\text{Benzoic acid.}}{C_6H_5.COOH}.$$

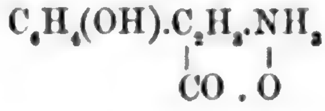
The amount of hippuric acid excreted in the urine in the case of man much depends on the nature of the diet: an increase in the amount of vegetable consumed causes a more or less marked increase, according to the nature of the vegetable; and in the case of the herbivora also much more is produced with certain kinds of food, such as grass, hay and straw, than with others, such as potatoes, swedes and fleshy roots. Moreover, when benzoic acid or substances which readily furnish benzoic acid on oxidation, such as toluene, benzaldehyde, cinnamic and quinic acids, are taken internally, they are excreted in the urine as hippuric acid. Substitution derivatives of benzoic acid, such as chloro-, amido-, hydroxy-, methoxy- and methylbenzoic acid are in like manner converted in their passage through the system into the corresponding derivatives of hippuric acid, even paranitrotoluene undergoing oxidation and conversion into paranitrohippuric acid when administered to dogs (Jaffé, *Deut. chem. Ges. Ber*, vii. 1673).

(1775) ALANINES or PROPANEGLYCINES: (?) $C_3H_7NO_2$ or $C_6H_{14}N_2O_4$.—*α-Alanine* is produced together with the compound homologous with diglycolamidic acid on boiling α-iodopropionic acid, $CH_2I.CH_2.COOH$, with an aqueous solution of ammonia, and crystallizes in colourless rhombic prisms very soluble in water; it has a sweet taste, and apparently is without action on vegetable colours. Cupric α-amidopropionate, $C_6H_{12}CuN_2O_4 + 5OH_2$, prepared by boiling a solution of α-alanine with cupric hydrate crystallizes in large dark-blue rhombic prisms, much more soluble than the cupric salt from β-alanine (Heintz, *ibid.*, clvi. 25). According to Mulder (*Deut. chem. Ges. Ber.*, ix. 1903), this alanine exhibits a slight acid reaction, and decomposes when heated with ammonia and acrylic acid.

β-Alanine may be prepared by digesting the product of the action of hydrocyanic acid on amidoethylic alcohol (aldehyde-ammonia) with hydrochloric acid (comp. pp. 737, 738); it is also formed on boiling β-chloropropionic acid with an aqueous or alcoholic solution of ammonia, but the amount produced is extremely small, the chloro-acid chiefly exchanging its chlorine for OH or OC_2H_5 (Heintz, *loc. cit.*). It crystallizes in tufts of rhombic prisms, and exhibits the closest resemblance in its properties to glycine. The cupric β-amidopropionate prepared from it crystallizes with only a single molecule of water.

(1776) **TYROSINE**: $C_9H_{11}NO_3$.—This compound is a product of the action of hydrating agents on various albumenoid substances, and occurs together with leucine in the pancreas and other parts of the animal organism, and also in cochineal and many of the lower forms of animal life. It is best prepared from horn shavings, which on the average yield about 4 per cent., by boiling with 2 pts. sulphuric acid and 8 pts. water for about 20 hours, then neutralizing the solution with milk of lime, concentrating, and rendering acid with acetic acid; the tyrosine which gradually separates out is purified by recrystallization from alcohol containing ammonia.

It crystallizes in fine glistening needles usually grouped in bundles, soluble in about 150 pts. of boiling water. It is characterized by furnishing a red precipitate on the addition of a solution of mercuric nitrate and a nitrite or nitrous acid: this precipitate has the composition $C_9H_9N_3O_7Hg_2$ (Thudichum and Wanklyn, *Journ. Chem. Soc*, xxii. 277), and is perhaps a nitroso-derivative. Like glycine, tyrosine forms crystalline compounds with acids, such as the hydrochloride $C_9H_{12}NO_3Cl$, and its alkaline solution has the property of dissolving cupric hydrate in the same relative proportion as glycine and leucine, but unlike glycine it is capable of exchanging two atoms of hydrogen for metals: thus on boiling its solution with cupric hydrate, the cupric derivative $(C_9H_{10}NO_3)_2Cu$ is produced, which crystallizes in dark-blue glistening needles soluble in 240 pts. boiling and 1230 pts. cold water, but the baric derivative formed by dissolving it in boiling baryta water has the composition $C_9H_9BaNO_3 + 2OH_2$. Tyrosine does not enter into reaction with ethylic iodide at 100° (212° F.) (Thudichum and Wanklyn). By the continued action of chlorinating agents, it is converted into tetrachloroquinone, $C_6Cl_4O_2$, and when fused with potassic hydrate, it yields paroxybenzoic acid, $C_6H_4(OH).COOH$ (Barth); it is decomposed by heating with a saturated solution of hydriodic acid at 140°—150° (284°—302° F.), its nitrogen being eliminated as ammonia (Hüfner): it would appear therefore that tyrosine is probably an oxyphenyl derivative either of α- or β-alanine; thus:



$$\begin{array}{l} C_6H_4(OH).C_2H_3.NH_2 \\ \qquad\qquad\quad | \qquad | \\ \qquad\qquad\quad CO\ .\ O \end{array}$$

(1777) **TETRANEGLYCINES**: (?) $C_4H_9NO_4$ or $C_8H_{18}N_2O_4$.—Only one glycine derived from butyric acid is known: it is formed by digesting the product of the action of bromine on butyric acid—consisting chiefly of ethylbromacetic acid, $CH_3.CH_2.CHBr.COOH$—with an aqueous or alcoholic solution of ammonia; it also occurs amongst the substances obtained on decomposing albumen by means of baric hydrate solution (Schützenberger). It crystallizes in glistening plates or tufts of needles, easily soluble in water, and like the other glycines has a sweet taste and is without action on vegetable colours (Schneider; Friedel and Machuca, *ibid.*, *Supp.* ii. 70).

(1778) **PENTANEGLYCINES**: (?) $C_5H_{11}NO_4$ or $C_{10}H_{22}N_2O_4$.—On heating isopropylbromacetic acid, $(CH_3)_2CH.CHBr.COOH$ (from isoprimary valeric acid), with ammonia (Fittig and Clarke, *ibid.*, cxxxix. 200; Schmidt and Sachtleben, *ibid.*, cxciii. 105), a glycine is produced which apparently is identical with the substance of the same formula isolated from the pancreas of the ox by Gorup-Besanez (*ibid.*, cxlii. 374; comp. Nencki, *Journ. pr. Chem.* [2], xv. 393), and as one of the products of the decomposition of albumen by baric hydrate (Schützenberger). It crystallizes in shining plates consisting of flat monoclinic prisms, and sublimes without previous fusion when carefully heated; it has no action on vegetable colours. On adding cupric acetate to its aqueous solution, the liquid becomes deep blue, and after a time, especially on warming, cupric amidoisovalerate separates in transparent scales.

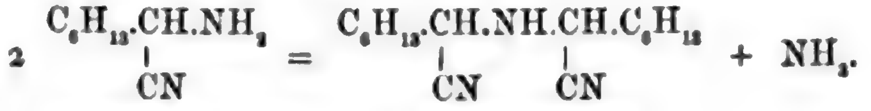
(1779) LEUCINES or HEXANEGLYCINES: (?) $C_6H_{13}NO_2$ or $C_{12}H_{26}N_2O_4$.—The leucines bear the same relation to the caproic or hexylic acids, $C_5H_{11}.COOH$, that glycine bears to acetic acid. At present only two of the many possible isomerides have been artificially prepared: one of these is obtained by the action of ammonia on the bromo-acid formed by heating caproic acid with bromine, and is therefore probably derived from normal butylbromacetic acid, $C_4H_9{}^n.CHBr.COOH$ (Hüfner, *Jour. pr. Chem.* [2], i. 6); the other has been prepared from the product of the action of hydrocyanic acid on the amidoamylic alcohol formed from valeral and ammonia (1634) by digesting it with hydrochloric acid (Limpricht; comp. Hüfner), and may therefore have been a mixture of two isomerides, although doubtless principally formed from the amidoamylic alcohol of the formula $(CH_3)_2CH.CH_2.CH(NH_2).OH$. According to Hüfner, the two products exhibit the closest similarity in most respects, but the former is only about half as soluble in cold water as the latter.

Leucine is one of the chief products of the action of hydrating agents on many albumenoids and animal substances, such as horn, fibrin, &c.; cervical ligament is said to yield from 38 to 45 per cent. when decomposed by boiling with 5 pts. of a mixture of 1 pt. sulphuric acid and 1½ pts. water. It is best purified by crystallization from alcohol containing ammonia, the last trace of colour being removed by crystallization from alcohol and water (Hofmeister). Leucine from horn, &c., forms soft nacreous scales consisting of concentrically grouped rhombic prisms; it is said to be tasteless, and to dissolve in about 27 pts. of cold water. Nencki, however, states that, by allowing ox-pancreas to putrefy, a leucine may be obtained which has a slightly sweetish taste, and requires 43·6 parts of water at 14°·5 (58°·1 F.) to dissolve it (*Journ. pr. Chem.*, [2], xv. 390). According to Hüfner, leucine from caproic acid dissolves in 107·5 pts., and that from valeral in 47·8 pts. of water at 12° (53°·6 F.), although the two products exactly resemble leucine from horn or fibrin in appearance, and furnish similar nitrates and cupric salts. From these few statements it will be evident that our knowledge of the leucines is extremely imperfect. The cupric amidocaproate obtained by boiling a solution of pure leucine (from horn) with cupric hydrate, is very difficultly soluble even in hot water, and crystallizes in delicate pale blue scales; it is much more soluble in solutions containing the cupric salts derived from the homologous glycines. Leucine, like glycine, has the property of preventing the precipitation of cupric hydrate by an alkali, no precipitate being formed on adding cupric sulphate to a solution of leucine in excess of sodic hydrate until the proportion $C_{12}H_{26}N_2O_4 : CuSO_4$ is exceeded (Hofmeister).

(1780) OCTANEGLYCINES: (?) $C_8H_{17}N_2O_2$ or $C_{16}H_{34}N_2O_4$.—Of the large number of glycines to be derived from the octylic acids, only one is known, viz., that obtained from the product of the action of hydrocyanic acid on the amido-alcohol formed from normal heptaldehyde and ammonia (1635).

The glycine thus prepared crystallizes in nacreous plates, and, like the other glycines, when carefully heated sublimes without melting; it dissolves in about 150 pts. of boiling water. It forms well crystallized compounds with acids.

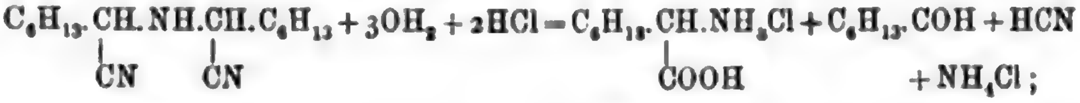
Erlenmeyer and Sigel (*Ann. Chem. Pharm.*, clxxvi. 341; clxxvii. 111) have shown that the amount of glycine thus produced is only equivalent to from ⅓ to ⅔rds, according to the condition of experiment, of the amount of heptaldehyde employed. The reasons for this are that a portion of the amido-cyanide which is formed by the action of the hydrocyanic acid on the amido-alcohol ($C_6H_{13}.CH(NH_2).OH + HCN = C_6H_{13}.CH(NH_2).CN + OH_2$), spontaneously undergoes decomposition into ammonia and imido-cyanide, the latter being at once produced in large quantity if the action be allowed to take place with too great violence; thus:



$$2\,\underset{\displaystyle CN}{C_6H_{13}.\overset{|}{CH}.NH_2} = \underset{\displaystyle CN\qquad\;\; CN}{C_6H_{13}.CH.NH.CH.C_6H_{13}} + NH_3.$$

Amidocaprylonitrile. Imidocaprylonitrile.

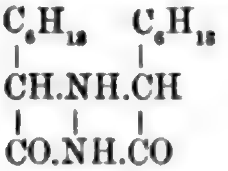
By boiling this imido-cyanide with a 20 per cent. solution of hydrochloric acid (b. p. 110° C.), or by heating it with 40 per cent. acid at 105° (221° F.), it is decomposed in the following manner:



$$\underset{\displaystyle CN\qquad CN}{C_6H_{13}.CH.NH.CH.C_6H_{13}} + 3OH_2 + 2HCl = \underset{\displaystyle COOH}{C_6H_{13}.CH.NH_3Cl} + C_6H_{13}.COH + HCN + NH_4Cl;$$

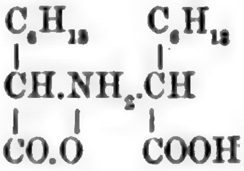
but by digesting it on the water bath with 40 per cent. acid, it is almost entirely converted into imidocaprylimide and imidocaprylic acid:

Imidocaprylimide



$$\begin{array}{ccc} C_6H_{13} & & C_6H_{13} \\ | & & | \\ CH.&NH.&CH \\ | & | & | \\ CO.&NH.&CO \end{array}$$

Imidocaprylic acid



$$\begin{array}{ccc} C_6H_{13} & & C_6H_{13} \\ | & & | \\ CH.&NH_2.&CH \\ | & | & | \\ CO.&O & COOH \end{array}$$

and these compounds are only decomposed by heating with 40 per cent. hydrochloric acid at 180° (356° F.). The amount of glycine obtained therefore depends entirely on the mode in which the amido-alcohol is acted upon by hydrocyanic acid and in which the product is treated with hydrochloric acid.

(1781) HYDROXY-ACIDS DERIVED FROM THE ACIDS OF THE ACETIC SERIES.—By the displacement of one or more atoms of hydrogen in the C_nH_{2n+1} radicle of the acids of the acetic series by the group OH a series of hydroxy-acids of the general formula $C_nH_{(2n+1-m)}(OH)_m.COOH$ are obtained, which obviously may be regarded as related to the alcohols of the form $C_nH_{(2n+1-m)}(OH)_m$ in precisely the same manner that the acids of the acetic series are related to the paraffins. A considerable number of monhydroxy-acids—so-called acids of the lactic series—have been obtained, but at present very few containing a greater number of hydroxyl groups are known, and most of these have been produced by oxidation of polyhydric alcohols such as glycerol and erythrol. The highest value for *m* in the above formula yet observed is 5, this being realized in the case of gluconic acid and its isomerides, $C_6H_8(OH)_5.COOH$.

The *hydroxy-acids* are much less stable compounds than the parent acids, most of them decomposing when distilled, and being readily oxidized; they are for the most part easily soluble in water. Those in which more than one hydroxyl group is associated with a single carbon atom, like the corresponding carbinols (comp. 1491), are only capable of existing under certain favourable conditions and cannot be isolated, although they may furnish perfectly stable derivatives.

The behaviour of these hydroxy-acids may be at once pictured if it be remembered that they are derivatives both of the acids of the acetic series and of the alcohols (carbinols) derived from the paraffins. Thus, like the acids of the acetic series, they exchange the hydrogen of the COOH group for metals when acted upon by metallic oxides, hydroxides and carbonates, but like the carbinols they do not furnish metallic derivatives stable in presence of water by the exchange for metals of hydrogen in the OH groups associated with the hydrocarbon radicle, although the hydrogen in these groups may be displaced by the more positive metals such as sodium by acting with the metal itself on the ethereal salts formed by the introduction of hydrocarbon radicles in place of the hydrogen in the COOH group; the compounds thus formed, however, like the analogous metallic derivatives of the carbinols, are decomposed by water and the metal displaced by hydrogen. Again, by the introduction of positive hydrocarbon radicles such as ethyl, C_2H_5, or of negative radicles such as acetyl, C_2H_3O, in place either of the hydrogen in the COOH group or of that in the OH groups associated with the hydrocarbon radicle, compounds are obtained which manifest the closest resemblance to those derived in a similar manner from the acids of the acetic series and the carbinols respectively. Thus the ethereal salts of the form $C_nH_{2n}(OH).COOC_mH_{2m+1}$, which may be prepared by the action of the carbinols on the hydroxy-acids in presence of hydrochloric acid, like those produced in a similar manner from the acids of the acetic series, are but very slightly affected by mere contact with cold water, although without difficulty decomposed by heating with water, especially in presence of an alkali or acid; the derivatives of the form $C_nH_{2n}(O.C_mH_{2m+1})$ COOH (*etheric acids*), however, like the ethers formed by displacing the hydrogen in the OH group of the carbinols by hydrocarbon radicles, are scarcely affected even when heated with alkalies. On the other hand, the compounds formed by the introduction of negative radicles such as acetyl in place of the hydrogen of the COOH group behave just as the acid anhydrides (1758), and are at once decomposed when brought into contact with cold water; whereas, if acetyl be introduced in place of the hydrogen of the hydroxyl groups associated with the hydrocarbon radicle, compounds are obtained which resemble the ethereal salts formed by similarly displacing the hydrogen in the OH groups of carbinols, being only slowly, if at all, acted upon by cold water. Further illustration of the double relationship of the hydroxy-acids is afforded by their behaviour with the haloid acids and haloid phosphorus compounds. When submitted to the action of the former, they exchange the OH groups associated with the hydrocarbon radicle for the equivalent amount of halogen, the hydroxyl present in the form of carboxyl remaining intact; when acted upon by the latter, however, all the hydroxyl groups present are displaced, but on bringing the compounds thus formed into contact with water the halogen which has displaced the OH group present as CO.OH is at once exchanged for hydroxyl.

In consequence of the similarity in the behaviour of the hydroxyl in hydroxy-acids which is directly associated with the hydrocarbon radicle of the acid, and of the hydroxyl in carbinols, the OH groups present in this condition in the hydroxy-acids generally are frequently spoken of as "alcoholic" hydroxyl groups. The number of alcoholic hydroxyl groups contained in a given acid may be ascertained by submitting it to the action of bodies such as acetic chloride or anhydride employed in excess, washing the product with water, and then ascertaining by analysis how many times the acetyl group is contained in the new substance; as above explained, the compound formed by the displacement of the hydrogen of the carboxyl group by acetyl is decomposed by mere contact with water, so that the number of acetyl groups contained in the product is equal to the number of alcoholic hydroxyl groups in the parent acid.

MONHYDROXY-ACIDS DERIVED FROM THE ACIDS OF THE ACETIC SERIES: ACIDS OF THE LACTIC SERIES.

(1782) The following acids of this series are known.

CH_2O_3	Hydroxyformic or carbonic acid	HO.COOH
$C_2H_4O_3$	Hydroxyacetic or glycolic acid	$CH_2(OH).COOH$
$C_3H_6O_3$	α-Hydroxypropionic or ethylenelactic acid	$CH_2(OH).CH_2.COOH$
	β-Hydroxypropionic or ethylidene-lactic acid	$CH_3.CH(OH).COOH$
$C_4H_8O_3$	α-Hydroxybutyric acid	$CH_2(OH).CH_2.CH_2.COOH$
	β-Hydroxybutyric acid	$CH_3.CH(OH).CH_2.COOH$
	γ-Hydroxybutyric acid	$CH_3.CH_2.CH(OH).COOH$
	Dimethhydroxyacetic or hydroxy-iso-butyric acid	$(CH_3)_2.C(OH).COOH$
$C_5H_{10}O_3$	Isoprophydroxyacetic acid	$(CH_3)_2CH.CH(OH).COOH$
	Methethhydroxyacetic acid	$CH_3.C(C_2H_5)(OH).COOH$
	γ-Meth-β-hydroxybutyric acid	$CH_3.CH(OH).CH(CH_3).COOH$
$C_6H_{12}O_3$	Hydroxycaproic or leucic acid	? $C_4H_9{}^{a}.CH(OH).COOH$
	Diethhydroxyacetic acid	$(C_2H_5)_2C(OH).COOH$
	γ-Eth-β-hydroxybutyric acid	$CH_3.CH(OH).CH(C_2H_5).COOH$
$C_7H_{14}O_3$	Isoamylhydroxyacetic acid	$C_5H_{11}.CH(OH).COOH$
	γ^2-Metheth-β-hydroxybutyric acid	$CH_3.CH(OH).C\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}.COOH$
$C_8H_{16}O_3$	Hexylhydroxyacetic acid	$C_6H_{13}{}^{a}.CH(OH).COOH$
	Diisopropylhydroxyacetic acid	$(C_3H_7)_2{}^{\beta}.C(OH).COOH$
$C_{12}H_{24}O_3$	γ-Dieth-β-hydroxybutyric acid	$CH_3.CH(OH).C(C_2H_5)_2.COOH$
	Diisoamylhydroxyacetic acid	$(C_5H_{11})_2.C(OH).COOH$

(1783) *Formation.*—Acids of the lactic series have been prepared by the following methods, which all appear to be of more or less general application.

1. By the direct oxidation of the corresponding acids of the acetic series, as in the formation of the first term (comp. 1807, 1808):

$$\underset{\text{Formic acid.}}{H.COOH} + (O + OH_2) = \underset{\text{Carbonic acid.}}{HO.COOH} + OH_2.$$

2. By the action of water either alone or in presence of metallic hydroxides on the monohaloid derivatives of the acids of the acetic series:

$$C_nH_{2n}X.COOH + OH_2 = C_nH_{2n}(OH).COOH + HX.$$
$$\underset{\text{Monochloracetic acid.}}{CH_2Cl.COOH} + OH_2 = \underset{\text{Hydroxyacetic acid.}}{CH_2(OH).COOH} + HCl.$$

The various isomeric and homologous haloid acids differ greatly in their behaviour under these circumstances, however, some being readily converted into the corresponding hydroxy-acids, while others are deprived of the elements of a molecule of haloid acid, and thus furnish an acid of the $C_nH_{2n-1}.COOH$ or acrylic series, just as the monohaloid derivatives of the paraffins are in some cases converted into the corresponding alcohol, and in others into hydrocarbons of the olefine series by the action of water or metallic hydroxides.

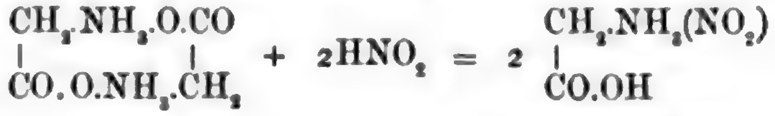
Corresponding "etheric acids" are frequently produced by the employment of an alcoholic solution of potassic hydroxide:

$$CBr(CH_3)_2.COOH + 2C_2H_5.OK = C(CH_3)_2(OC_2H_5).COOK + KBr + C_2H_5.OH;$$

Dimethbromacetic acid. Potassic dimethethoxyacetate.

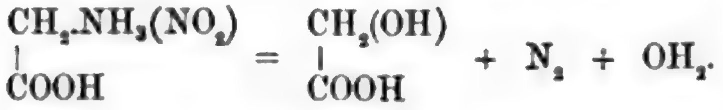
and, similarly, by the action of compounds such as potassic thiohydrate, KSH, and thioethylate, KSC_2H_5, analogous thio-acids are obtained.

3. By the action of nitrous acid on the glycines (1771); thus:



$$\begin{array}{l} CH_2.NH_3.O.CO \\ |\qquad\qquad\quad | \\ CO.O.NH_3.CH_2 \end{array} + 2HNO_2 = 2\begin{array}{l} CH_2.NH_3(NO_2) \\ | \\ CO.OH \end{array}$$

Glycine. Amidacetic nitrite.



$$\begin{array}{l} CH_2.NH_3(NO_2) \\ | \\ COOH \end{array} = \begin{array}{l} CH_2(OH) \\ | \\ COOH \end{array} + N_2 + OH_2.$$

4. By oxidation of the glycols of the form $C_nH_{2n}(OH).CH_2(OH)$ by dilute nitric acid or free oxygen in presence of platinum black:

$$C_nH_{2n}(OH).CH_2(OH) + 2(O + OH_2) = C_nH_{2n}(OH).COOH + 3OH_2.$$

$$CH_3.CH(OH).CH_2(OH) + 2(O + OH_2) = CH_3.CH(OH).COOH + 3OH_2$$

Propyleneglycol. Lactic acid.

5. By combining the aldehydes of the form $C_nH_{2n+1}.COH$ and the ketones of the form $(C_nH_{2n+1})_2CO$ with hydrocyanic acid, and digesting the resulting hydroxycyanides with hydrochloric acid:

$$C_nH_{2n+1}.COH + HCN = C_nH_{2n+1}.CH(OH).CN;$$

$$C_nH_{2n+1}.CH(OH).CN + 2OH_2 + HCl = C_nH_{2n+1}.CH(OH).COOH + NH_4Cl.$$

$$CH_3.COH + HCN = CH_3.CH(OH).CN$$

Ethaldehyde. Cyanethylic alcohol.

$$CH_3.CH(OH).CN + 2OH_2 + HCl = CH_3.CH(OH).COOH + NH_4Cl.$$

Cyanethylic alcohol. Lactic acid.

$$(C_nH_{2n+1})_2CO + HCN = (C_nH_{2n+1})_2C(OH).CN;$$

$$(C_nH_{2n+1})_2CH(OH).CN + 2OH_2 + HCl = (C_nH_{2n+1})_2C(OH).COOH + NH_4Cl$$

$$(CH_3)_2CO + HCN = (CH_3)_2C(OH).CN;$$

Dimethylketone. Cyanodimethylcarbinol.

$$(CH_3)_2C(OH).CN + 2OH_2 + HCl = (CH_3)_2C(OH).COOH + NH_4Cl.$$

Cyanodimethylcarbinol. Dimethhydroxyacetic acid.

6. By the action of nascent hydrogen on ketonic acids of the form $C_nH_{2n-1}O.COOH$:

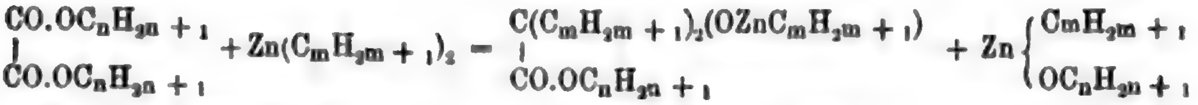
$$C_nH_{2n+1}.CO.C_nH_{2n}.COOH + 2H = C_nH_{2n+1}.CH(OH).C_nH_{2n}.COOH.$$

$$CH_3.CO.COOH + 2H = CH_3.CH(OH).COOH.$$

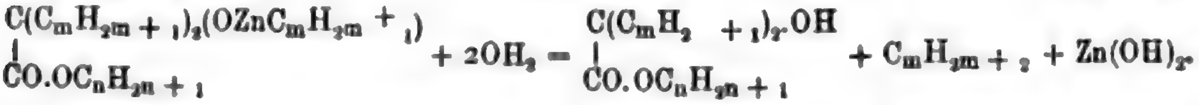
Acetoacetic acid. Methhydroxyacetic acid.

7. By the action of the zinc organo-metallic compounds on ethereal salts of oxalic acid, the product being treated with water.

Frankland and Duppa, by whom this important method was discovered, represented the reaction by equations of the following form (*Phil. Trans.*, 1866, p. 313):

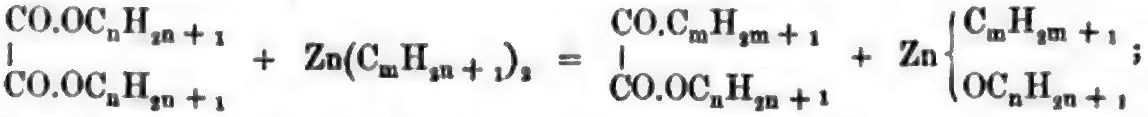


$$\begin{array}{l}CO.OC_nH_{2n+1}\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn(C_mH_{2m+1})_2 = \begin{array}{l}C(C_mH_{2m+1})_2(OZnC_mH_{2m+1})\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn\begin{cases}C_mH_{2m+1}\\ OC_nH_{2n+1}\end{cases}$$



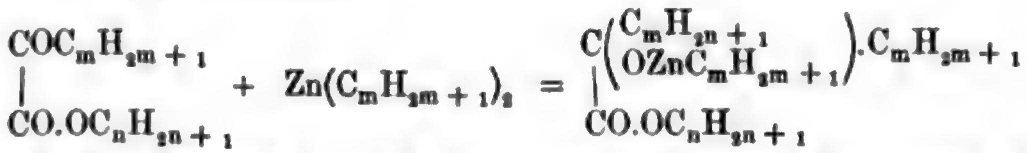
$$\begin{array}{l}C(C_mH_{2m+1})_2(OZnC_mH_{2m+1})\\ |\\ CO.OC_nH_{2n+1}\end{array} + 2OH_2 = \begin{array}{l}C(C_mH_2\;{+}_1)_2.OH\\ |\\ CO.OC_nH_{2n+1}\end{array} + C_mH_{2m+2} + Zn(OH)_2.$$

It may be suggested, however, that the reaction more probably takes place in such a manner that in the first instance one of the OC_nH_{2n+1} groups of the oxalate is displaced by the radicle of the zinc compound, thus:



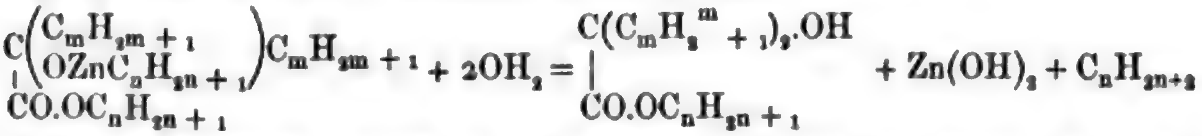
$$\begin{array}{l}CO.OC_nH_{2n+1}\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn(C_mH_{2n+1})_2 = \begin{array}{l}CO.C_mH_{2m+1}\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn\begin{cases}C_mH_{2m+1}\\ OC_nH_{2n+1}\end{cases};$$

and that the product of this reaction then enters into reaction with a second molecule of the zinc compound:

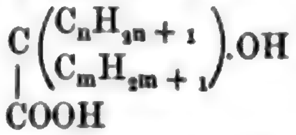


$$\begin{array}{l}COC_mH_{2m+1}\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn(C_mH_{2m+1})_2 = \begin{array}{l}C\left(\begin{array}{l}C_mH_{2n+1}\\ OZnC_mH_{2m+1}\end{array}\right).C_mH_{2m+1}\\ |\\ CO.OC_nH_{2n+1}\end{array}$$

It may be that the order in which these reactions occur is the reverse of that here supposed, or they may even occur simultaneously (comp. 1810). The subsequent action of water is expressed by the equation:

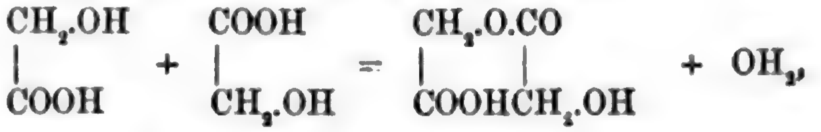


$$\begin{array}{l}C\left(\begin{array}{l}C_mH_{2m+1}\\ OZnC_nH_{2n+1}\end{array}\right)C_mH_{2m+1}\\ |\\ CO.OC_nH_{2n+1}\end{array} + 2OH_2 = \begin{array}{l}C(C_mH_2{}^m\;{+}_1)_2.OH\\ |\\ CO.OC_nH_{2n+1}\end{array} + Zn(OH)_2 + C_nH_{2n+2}$$

It is not necessary to prepare the zinc compound, but the oxalate may be at once brought into contact with zinc and the iodide of the radicle which it is required to introduce; and even a mixture of two iodides may be employed, ethereal salts of acids of the form  $\begin{array}{l}C\left(\begin{array}{l}C_nH_{2n+1}\\ C_mH_{2m+1}\end{array}\right).OH\\ |\\ COOH\end{array}$ being then produced.

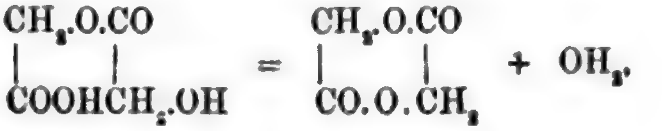
(1784) *Properties.*—Allusion has already been made to some of the properties of these acids, and the following need here only be mentioned.

1. The majority of the acids of the lactic series cannot be distilled unchanged, but the nature of the change which they undergo depends on their constitution. For example, when hydroxyacetic or glycolic acid is heated on the water bath, it is gradually converted into dehydroglycolic acid:



$$\begin{array}{l}CH_2.OH\\ |\\ COOH\end{array} + \begin{array}{l}COOH\\ |\\ CH_2.OH\end{array} = \begin{array}{l}CH_2.O.CO\\ |\qquad\;\; |\\ COOHCH_2.OH\end{array} + OH_2,$$

and on continued heating, this compound loses the elements of a molecule of water and is converted into the "etheric-anhydride" *glycolide*:



$$\begin{array}{l}CH_2.O.CO\\ |\qquad\;\; |\\ COOHCH_2.OH\end{array} = \begin{array}{l}CH_2.O.CO\\ |\qquad\;\; |\\ CO.O.CH_2\end{array} + OH_2.$$

Methyl-, ethyl- and isopropyl-hydroxyacetic acids behave in a similar manner, but dimethhydroxyacetic acid, $(CH_3)_2C(OH).COOH$, may be distilled unchanged. α-Hydroxypropionic (hydracrylic) acid, the isomeride of methylhydroxyacetic or lactic acid, however, yields acrylic acid on distillation: $CH_2(OH).CH_2.COOH = CH_2{=}CH.COOH + OH_2$; and the homologous acids of the form $R'.CH(OH).CH_2.COOH$, $CH_2(OH).CH(R').COOH$ and $R'.CH(OH).CH(R').COOH$ in like manner furnish the corresponding homologues of acrylic acid. A third mode of decomposition is illustrated by the conversion of γ-diethyl-β-hydroxybutyric acid into diethacetic acid and ethaldehyde:

$$CH_3.CH(OH).C(C_2H_5)_2.COOH = CH_3.COH + CH(C_2H_5)_2.COOH.$$

2. When heated with a concentrated aqueous solution of hydriodic acid, they are converted into the corresponding acids of the acetic series, the reaction doubtless taking place in two stages, thus:

$$\underset{\text{Lactic acid.}}{CH_3.CH(OH).COOH} + HI = \underset{\text{Iodopropionic acid.}}{CH_3.CHI.COOH} + OH_2;$$

$$\underset{\text{Iodopropionic acid.}}{CH_3.CHI.COOH} + HI = \underset{\text{Propionic acid.}}{CH_3.CH_2.COOH} + I_2.$$

3. They are readily oxidized, especially by a mixture of potassic dichromate and diluted sulphuric acid. From the results hitherto obtained it would appear that in most cases they behave as the corresponding carbinols, those which contain the group $CH_2.(OH)$ furnishing the corresponding dibasic acids owing to the conversion of this group into COOH (comp. p. 886); while those containing the group $CH.(OH)$ are first converted into dihydroxy-acids which at once undergo oxidation to products containing fewer carbon atoms, thus:

$$\left.\begin{matrix}C_nH_{2n+1}\\COOH\end{matrix}\right\}CH.OH + (O + OH_2) = \left.\begin{matrix}C_nH_{2n+1}\\COOH\end{matrix}\right\}C(OH)_2 + OH_2;$$

$$\left.\begin{matrix}C_nH_{2n+1}\\COOH\end{matrix}\right\}C(OH)_2 + (O + OH_2) = C_nH_{2n+1}.C(OH)_3 + HO.COOH;$$

those containing the group C(OH) being acted upon in the following manner:

$$\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\\COOH\end{matrix}\right\}C(OH) + (O + OH_2) = \left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\}C(OH)_2 + HO.COOH.$$

(1785) **Hydroxyformic or Carbonic Acid**: $H_2CO_3{=}CO(OH)_2$.—The preparation and properties of this acid need not here be described.

(1786) *Metallic and Ethereal Carbonates.*—Although itself extremely unstable, carbonic acid furnishes many stable metallic and ethereal salts; but unlike all the other acids of the lactic series, it behaves as a dibasic acid, exchanging with equal facility both atoms of hydrogen for the equivalent amount of metal; this behaviour, however, is perfectly in accordance with its constitution, since both the hydroxyl groups which it contains are, it must be supposed, directly associated with the negative radicle CO, whereas in the homologous acids, which are represented by the general formula $C_nH_{2n}(OH).COOH$, only one of the OH groups is directly influenced by the CO group, the other being associated with a positive hydrocarbon radicle.

Acid metallic carbonates of the form $HM'CO_3$, normal carbonates of the form M'_2CO_3, and a number of so-called basic carbonates are known. The basic carbonates may be viewed in two ways: either as formed by the partial displacement of the hydrogen in the hydroxides of polyvalent metals by the radicle CO; or as derivatives of so-called *orthocarbonic acid*,* $C(OH)_4$. Thus malachite, $H_2Cu_2CO_5$, may be represented either as a basic carbonate of the formula $(HO.Cu)'_2CO_3$, or as cupric orthocarbonate with a single molecule of water of crystallization, $Cu_2CO_4 + OH_2$; both classes of compounds probably exist, and there are also carbonates which may be regarded as salts of polycarbonic acids of the forms $xH_2CO_3 - yOH_2$ and $xH_4CO_4 - yOH_2$. The acid metallic carbonates are readily decomposed into normal carbonate, carbonic anhydride and water; the normal carbonates of the more positive metals such as potassium, sodium, and barium withstand very high temperatures, but those containing less positive metals are more or less readily decomposed by heat.

Acid ethereal salts of carbonic acid do not exist, but metallic ethereal carbonates are formed by the direct union of carbonic anhydride with the metallic derivatives of the monhydric carbinols, thus: $CO_2 + NaOC_nH_{2n+1} = CO_3Na.C_nH_{2n+1}$; and by the action of the hydroxides of the more positive metals on the normal ethereal carbonates in accordance with the equation: $CO_3(C_nH_{2n+1})_2 + KOH = CO_3K.C_nH_{2n+1} + C_nH_{2n+1}OH$. These salts are readily decomposed by water, yielding the corresponding alcohol and acid metallic carbonate.

Normal ethereal carbonates may be produced in a variety of ways, amongst others by the action of compounds such as ethylic iodide on argentic carbonate or the metallic ethereal carbonates, the latter method being available for the preparation of mixed salts; and by the action of carbonic chloride, $COCl_2$, on the alcohols or their sodium derivatives. The following may be quoted as examples:

Ethylic carbonate: $(C_2H_5)_2CO_3$.—This compound is formed in considerable quantity as a bye-product in the preparation of ethylic oxalate from alcohol and oxalic acid, and may also be prepared by the action of sodium or sodic ethylate on ethylic oxalate (q. v.). It is a mobile, colourless liquid of pleasant ethereal

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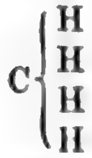
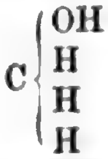
* Orthocarbonic acid belongs to the class of "acidhydrols" (foot-note, p. 823), bearing the same relation to carbonic acid that orthoformic acid bears to formic acid. Its ethylic derivative $C(OC_2H_5)_4$, is a perfectly stable compound, boiling without the slightest change at about 160° (316°·4 F.); it is obtained by digesting trichloronitromethane (chloropicrin) with an alcoholic solution of sodic ethylate (Bassett). Orthocarbonic acid may be regarded as the last term in the series of hydroxides formed by the gradual oxidation of methane; thus:



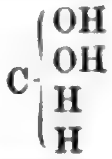
$$C\begin{cases}H\\H\\H\\H\end{cases}$$

Methane.



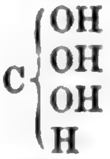
$$C\begin{cases}OH\\H\\H\\H\end{cases}$$

Methylic alcohol.



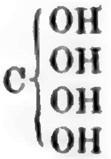
$$C\begin{cases}OH\\OH\\H\\H\end{cases}$$

Methaldehydrol.



$$C\begin{cases}OH\\OH\\OH\\H\end{cases}$$

Orthoformic acid.



$$C\begin{cases}OH\\OH\\OH\\OH\end{cases}$$

Orthocarbonic acid.

odour, boiling at 126° (258°·8 F.), almost insoluble in water, but slowly decomposed when left in contact with it, and rapidly decomposed by alkalies.

Phenylic carbonate: $(C_6H_5)_2CO_3$, is obtained together with the chlorocarbonate $ClCO.OC_6H_5$ on heating phenol with carbonic chloride in sealed tubes at about 150° (302° F.); it is a crystalline body, melting at 78° (172°·4 F.) (Kempf, *Jour. pr. Chem.* [2], i. 405).

(1787) COMPOUNDS FORMED BY THE DISPLACEMENT OF ONE OF THE OH GROUPS IN CARBONIC ACID.—By the displacement of one of the OH groups in carbonic acid by radicles such as Cl, CN, and NH_2, compounds are obtained, which are, in reality, substitution derivatives of formic acid, but they are perhaps more conveniently considered in connexion with carbonic acid.

(1788) ETHEREAL CHLOROCARBONATES.—These compounds are formed by the action of carbonic chloride on the alcohols in accordance with the equation: $COCl_2 + HOR' = ClCO.OR' + HCl$. They are colourless, pungent smelling liquids, which decompose in contact with water.

Ethylic chloroformate (*chlorocarbonate*): $ClCO.OC_2H_5$: is obtained by passing carbonic chloride into anhydrous alcohol; the product is rapidly washed with cold water, dried over calcic chloride, and the chloroformate separated from the ethylic carbonate which is simultaneously produced in small quantity by fractional distillation. It is a colourless mobile liquid of sp. gr. 1·139 at 15° (59° F.), which boils unchanged at 94° (201°·2 F.); its vapour has a most irritating effect on the eyes and nose. When heated to a temperature of about 150° (302° F.), it is decomposed into carbonic anhydride and monochlorethane; and metallic sodium causes its conversion into ethylic carbonate: $2ClCO.OC_2H_5 + 2Na = CO(OC_2H_5)_2 + CO + 2NaCl$; hence it is of little service in effecting the introduction of the group $COOC_2H_5$ into hydrogenized carbon compounds (Wilm and Wischin, *Ann. Chem. Pharm.*, cxlvii. 150).

Little is known of the homologues of ethylic chloroformate. The methylic derivative is probably one of the products of the action of chlorine on methylic formate (Henry, *Deut. chem. Ges. Ber.*, vi. 742). The higher homologues appear to be very unstable bodies, since both isobutylic and isamylic chloroformate are decomposed on distillation; they are also very readily decomposed by water, and converted into the corresponding carbonates, thus: $Cl.COOC_4H_9{}^{\beta} + OH_2 = HO.COOC_4H_9 + HCl$; $2HO.COO_4H_9 = CO(OC_4H_9)_2 + CO_2 + OH_2$.

(1789) ETHYLIC CYANOFORMATE (CYANOCARBONATE): $NC.COOC_2H_5$, was first obtained by distilling ethylic oxamate with phosphoric anhydride (Weddige): $P_2O_5 + CO(NH_2).COOC_2H_5 = NC.COOC_2H_5 + {}_2HPO_3$; according to Wallach (*Ann. Chem. Pharm.*, clxxxiv. 7), it is best prepared by the action of phosphoric pentachloride: $CO(NH_2).COOC_2H_5 + PCl_5 = CCl_2(NH_2).COOC_2H_5 + POCl_3$; $CCl_2(NH_2).COOC_2H_5 = 2HCl + CN.COOC_2H_5$. Ethylic cyanoformate is a mobile colourless liquid, having an ethereal but pungent odour; it boils at 116° (240°·8 F.) It slowly decomposes in contact with cold water, and rapidly on heating, into alcohol, hydrocyanic acid, and carbonic anhydride: alkalies have a similar action; if left in contact with concentrated hydrochloric acid, however, it is entirely converted into oxalic acid, alcohol, and ammonic chloride. It is very readily acted upon by ammonia and converted into ethylic amidoformate (urethane), $NH_2.COOC_2H_5$, and ammonic cyanide; substituted amines have a similar action. It combines directly with hydric sulphide, forming the compound $CS(NH_2).COOC_2H_5$. If heated with a small quantity of bromine at a temperature not exceeding 120° (248° F.), it undergoes a remarkable change, being converted into a crystalline polymeride. It undergoes a similar change slowly at ordinary temperatures, and more rapidly on heating, if saturated with hydrochloric acid gas. This polymeride crystallizes in well-developed six-sided prisms, difficultly soluble in water, alcohol, and benzene; it melts at 165°

(329° F.), but decomposes if heated above this temperature. On treatment with hydrochloric acid, it furnishes ethylic alcohol, oxalic acid, and ammonic chloride, and is similarly decomposed by boiling with alkalies; but if dissolved in a cold solution of potassic hydrate, it is converted into the corresponding potassic derivative, which may be obtained crystallized in long needles by allowing the solution to evaporate spontaneously. Ammonia produces a similar change, displacing the OC_2H_5 group by NH_2.

Methylic and isobutylic cyanoformate are formed from the corresponding oxamates on distillation with phosphoric anhydride; the former boils at about 100° (212° F.), and is more easily decomposed by water, the latter at 146° (294°·8 F.), and is less easily decomposed by water than the ethylic compound. Both gradually undergo polymerization when saturated with hydrochloric acid gas (Weddige, *Jour. pr. Chem.* [2], x. 193).

(1790) AMIDOFORMIC OR CARBAMIC ACID: $NH_2.COOH$.—This acid is not known in the free state, but both metallic and ethereal salts derived from it are readily obtained; the latter are usually spoken of as *urethanes*. The metallic salts have recently been submitted to careful investigation by Drechsel (*Journ. pr. Chem.* [2], xvi. 180).

Ammonic carbamate: $NH_2.COONH_4$, apparently is always formed whenever carbonic anhydride and ammonia are brought together either in the anhydrous condition or in presence of water; it is a constituent of ordinary commercial ammonic carbonate. To prepare it in a pure state, ammonia and carbonic anhydride are simultaneously passed into anhydrous alcohol which is kept cool; small crystals soon form in the liquid, and when sufficient has been produced, the crystals together with the alcohol are enclosed in tubes which are heated for a short time to 100°—110° (212°—230° F.), and then allowed to cool slowly; during the cooling, it crystallizes out in large thin plates, which are separated from the liquid, rapidly pressed between bibulous paper and dried over potassic hydrate (Basaroff, *ibid.*, i. 283). Ammonic carbamate undergoes decomposition in contact with water, in which it is easily soluble, being converted into normal ammonic carbonate, but this change takes place only gradually, especially if ammonia be present (Drechsel); on the other hand, however, ammonic carbonate dissolved in water is partially converted into carbamate on standing (Divers; Drechsel. For the method of detecting carbamate in presence of carbonate see Drechsel, *ibid.*, p. 170).

Calcic carbamate: $(NH_2.CO_2)_2Ca + 2OH_2$ (comp. Drechsel).—The behaviour of this salt is in many respects of interest. When water is poured over it, at first a perfectly clear solution is obtained, but within about half a minute the liquid becomes opalescent from the separation of calcic carbonate; a much more stable solution is obtained by dissolving the salt in a solution of ammonia, the tendency to decompose being less the more concentrated the ammonia solution; by saturating a warm ammoniacal solution with the salt and then cooling it to 0° (32° F.), it may be obtained in magnificent four-sided prisms 1–2 min. in length.

The metallic carbamates apparently are in the first instance all converted into the corresponding cyanates when heated: $NH_2.COOM = NCOM + OH_2$; but these frequently undergo further change: thus, ammonic carbamate yields urea (Basaroff); and the carbamates of the alkaline earth metals are converted into the corresponding metallic derivatives of cyanamide $NH_2.CN$ (Drechsel).

Ethylic amidoformate or carbonate; urethane: $NH_2.COOC_2H_5$.—This compound may be formed by the action of ammonia on ethylic chloroformate (chlorocarbonate): $Cl.COOC_2H_5 + 2NH_3 = NH_2.COOC_2H_5 + NH_4Cl$, or on ethylic carbonate: $CO(OC_2H_5)_2 + NH_3 = NH_2.COOC_2H_5 + HOC_2H_5$; other methods of preparation will be described later on.

It crystallizes very readily from alcohol in large transparent prisms, melting at 52° (125°·6 F.), and boils without alteration at about 180° (356° F.); it is much more stable in presence of water than the metallic carbamates.

The homologous compounds closely resemble the ethylic salt. *Methylic carbamate* melts at about 55° (131° F.), and boils at 177° (350°·6 F.); *propylic carbamate* melts at 50° (122° F.) (Cahours); *isobutylic carbamate* melts at 55° (131° F.) and boils at 207° (404°·6 F.) (Mylius, *Deut. chem. Ges. Ber.*, v. 973); *isamylic carbamate* melts at 66° (150°·8 F.), and boils at about 220° (428° F.).

(1791) THIOCARBONIC ACIDS AND THEIR DERIVATIVES.—Thiocarbonic anhydride (carbonic bisulphide) enters into reaction with metallic thiohydrides (sulphydrates) and sulphides in precisely the same manner that carbonic anhydride does with metallic hydroxides (hydrates) and oxides, forming metallic thiocarbonates (sulphocarbonates), thus:

$$\mathrm{CO_2 + 2KOH = CO(OK)_2 + OH_2.}$$
$$\mathrm{CS_2 + 2KSH = CS(SK)_2 + SH_2.}$$

Bodies intermediate in composition between the carbonates and these thiocarbonates are probably formed by the action of metallic hydroxides on carbonic oxysulphide and bisulphide, thus: $\mathrm{CS_2 + 2KOH = K_2COS_2 + OH_2}$, but they have not been isolated. On treatment with dilute hydrochloric acid, the thiocarbonates furnish thiocarbonic acid, $\mathrm{CS(SH)_2}$, as an oily liquid; by boiling their aqueous solutions they are rapidly converted into carbonates, a similar decomposition taking place at ordinary temperatures: $\mathrm{K_2CS_3 + 3OH_2 = K_2CO_3 + 3SH_2}$.

Carbonic anhydride, however, not only combines with metallic hydroxides and metallic derivatives of the carbinols, but also with metallic derivatives of thiocarbinols; and in like manner, carbonic oxysulphide and bisulphide unite with metallic derivatives of the carbinols forming crystalline metallic ethereal salts of thiocarbonic acids. Thus carbonic oxysulphide and bisulphide unite with potassic ethylate forming the compounds $\mathrm{CO(OC_2H_5).SK}$ and $\mathrm{CS(OC_2H_5).SK}$ respectively; on treatment with hydrochloric acid, the former is at once decomposed with evolution of carbonic oxysulphide (Salomon, *Jour. pr. Chem.* [2], v. 476), but the latter yields the acid ethylic salt—*xanthic acid*, $\mathrm{C_2H_5O.CS.SH}$, as a colourless, heavy oil, insoluble in water. By the action of iodine on these metallic ethereal salts, the metal is withdrawn and compounds resulting from the residues of two molecules of the salt are produced, potassic xanthate, for example, being acted upon thus: $\mathrm{2C_2H_5O.CSSK + I_2 = (C_2H_5O.CS.S)_2 + 2KI}$.

The oxygen in the normal ethereal salts of carbonic acid may also be partially or wholly displaced by sulphur. Thus the following complete series of thio-derivatives of ethylic carbonate is known (comp. Salomon, *ibid.*, vi. 433):

	B. P. ° C.	Sp. Gr. at 19° C.
$\mathrm{CO}\left\{\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix}\right.$	156	1·0285
$\mathrm{CS}\left\{\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{matrix}\right.$	161	1·0325 (?)
$\mathrm{CO}\left\{\begin{matrix}\mathrm{SC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix}\right.$	196	1·085
$\mathrm{CS}\left\{\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix}\right.$	200	1·085
$\mathrm{CS}\left\{\begin{matrix}\mathrm{SC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix}\right.$	240	1·152

The methods of preparing these compounds are as follows:

I. $CO\left\{\begin{array}{l}OC_2H_5\\SC_2H_5\end{array}\right.$, by the action of ethylic chloroformate on sodic thioethylate, $C_2H_5.SNa$; and by the action of ethylic bromide on the salt $CO(OC_2H_5).SK$ (Salomon).

II. $CS(OC_2H_5)_2$, by heating the compound $(S.CS.OC_2H_5)_2$ (Debus).

III. $CO(SC_2H_5)_2$, by the action of sulphuric acid on ethylic thiocyanate, $NC.SC_2H_5$ (Schmitt and Glutz), and by the action of carbonic chloride on sodic thioethylate (Salomon).

IV. $CS\left\{\begin{array}{l}OC_2H_5\\SC_2H_5\end{array}\right.$, by the action of ethylic chloride, bromide or iodide on potassic xanthate, $CS(OC_2H_5).SK$ (Debus, Salomon).

V. $CS(SC_2H_5)_2$, by the action of ethylic chloride, bromide or iodide on potassic thiocarbonate (Schweitzer, Husemann).

They are mobile liquids of unpleasant odour. Those which contain the radicle CO, like ethylic carbonate, furnish ethylic carbamate $NH_2.COOC_2H_5$, or urea CON_2H_4, on digestion with ammonia; whereas those containing the radicle CS finally yield ammonic thiocyanate. Their behaviour with an alcoholic solution of potassic hydrate is in some respects peculiar, since those containing the radicle CO form potassic carbonate, whereas those containing the radicle CS form the salt $CO(OC_2H_5).SK$; it may be supposed that the decomposition of the thiocarbonate is not immediately effected by the potassic hydrate, but that an orthothiocarbonate is first produced by their combination and subsequently decomposed; thus:

$$CS\left\{\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}\right. + KOH = C\left\{\begin{array}{l}(OC_2H_5)_2\\OH\\SK\end{array}\right. = CO\left\{\begin{array}{l}OC_2H_5\\SK\end{array}\right. + C_2H_5.OH.$$

The isomeric methylic ethylic dithiocarbonates

$$CH_3S.CS.OC_2H_5 \text{ and } CH_3O.CS.SC_2H_5$$

behave in a similar manner, both being converted into the same ethylic salt, $KS.COOC_2H_5$, by the action of potassic ethylate, and into the corresponding methylic salt, $KS.COOCH_3$, by the action of potassic methylate; the latter salt is even converted into the ethylic salt by mere boiling with ethylic alcohol, but the reverse change has not been effected (Salomon, *ibid.*, viii. 114).

Carbonic oxysulphide and bisulphide behave like carbonic anhydride with ammonia, combining directly with it to form crystalline ammonic thiocarbonates; that produced from carbonic oxysulphide has the formula $NH_2.CO.SNH_4$: on treatment with dilute acids, it at once decomposes with evolution of carbonic oxysulphide; when heated alone at about 140° (284° F.), it is converted into urea, CON_2H_4 (Kretzschmar, *ibid.*, viii. 474). The ammonic salt produced by the union of ammonia and carbonic bisulphide, when treated with dilute hydrochloric acid, furnishes the corresponding acid, $NH_2.CSSH$, as a heavy oily liquid capable of decomposing metallic carbonates with effervescence; by the action of the halogens, it is converted into so-called ***hydranzotin***, $(NH_2.CS.S)_2$, a crystalline body of considerable stability (*Jour. Chem. Soc.*, 1878, p. 857).

Ethereal salts of thiocarbamic acids may be obtained by methods similar to those by which ethereal salts of carbamic acid are formed, and they closely resemble these latter in their properties; thus the following complete series of thio-derivatives of ethylic carbamate are known:

I. $NH_2.CO.SC_2H_5$, obtained by the action of gaseous ammonia on the compound $ClCO.SC_2H_5$, produced by saturating thioethylic alcohol with carbonic chloride; it melts at 108° (226°·4 F.) (Salomon, *ibid.*, vii. 252).

II. $NH_2.CS.OC_2H_5$, obtained by the action of ammonia on the thiocarbonate $C_2H_5S.CS.OC_2H_5$ and on the compound $(C_2H_5O.CSS)_2$; it melts at 38° (100°·4 F.).

III. $NH_2.CS.SC_2H_5$, produced by the direct combination of hydric sulphide and ethylic thiocyanate: $NC.SC_2H_5 + SH_2 = NH_2.CS.SC_2H_5$ (Conrad and Salomon, *ibid.*, x. 28); it melts at about 42° (107°·6 F.). When decomposed with potassic hydrate, the first of these compounds yields potassic carbonate, but the two others furnish potassic thiocyanate.

(1792) HYDROXYACETIC OR GLYCOLIC ACID; *Glycolic acid; oxyacetic acid*: $C_2H_4O_3 = CH_2(OH).COOH$.—This acid is formed by the action of water on the monohaloid derivatives of acetic acid (comp. 1794); by the action of nitrous acid on glycine; by oxidation of ethylic alcohol, ethaldehyde, glycol and other hydroxy-compounds, such as glycerol, levulose (q.v.), &c.; by the action of nascent hydrogen on oxalic acid (Schulze, Church, Claus) or ethylic oxalate (Eghis, Debus); and by the action of alkalies on glyoxal and glyoxylic acid (Debus). It has been detected in the juice of unripe grapes (Erlenmeyer), and in the leaves of the Virginia creeper—*Ampelopsis hederacea* (Gorup-Besanez). It is best prepared by boiling a moderately concentrated aqueous solution of monochloracetic acid for several hours in a flask attached to a reversed condenser, and then evaporating the solution to a syrup on the water-bath to expel the hydrochloric acid (Fittig, *Deut. chem. Ges. Ber.*, ix. 1197).

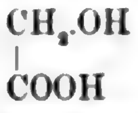
Hydroxyacetic acid crystallizes from water, in which it is very soluble, in concentrically grouped needles; on dissolving these in ether free from alcohol and allowing the solution to slowly evaporate *in vacuo*, it separates in anhydrous non-deliquescent plates melting at 80° (176° F.) (Fahlberg, *Jour. pr. Chem.* [2], vii. 329). It is very easily reduced to acetic acid by heating with hydriodic acid solution (Kekulé), and may also be converted into this acid by prolonged digestion with zinc and dilute sulphuric acid (Claus, *Ann. Chem. Pharm.*, cxlv. 256). When heated with a saturated solution of hydrobromic acid at 100° (212° F.), it yields bromacetic acid (Kekulé), but, according to Fahlberg, hydrochloric acid is without action under similar circumstances. It is by no means readily acted upon by phosphoric pentachloride: on heating a mixture of the two substances in simple molecular proportions to about 80° (176° F.), hydroxyacetic chloride, $CH_2(OH).COCl$, is apparently produced; if double the quantity of pentachloride be employed, and the mixture heated at 120° (248° F.), monochloracetic chloride is formed (Fahlberg). It is very readily oxidized and converted into oxalic acid. When heated with sulphuric acid, it is decomposed in accordance with the equation: $CH_2(OH).COOH + OH_2 = CH_2(OH)_2 + H.COOH$ (comp. 1624).

Metallic and Ethereal Salts.—Hydroxyacetic acid furnishes a number of characteristic crystalline metallic salts. *Calcic hydroxyacetate*, $[CH_2(OH)CO_2]_2Ca$, crystallizes with 2 mols. of water in glistening concentrically grouped needles, soluble in 80 pts. water at 15° (59° F.), and in anhydrous much less soluble aggregates (Fahlberg; Carius, *ibid.*, ix. 303). *Cupric hydroxyacetate*, $[CH_2(OH).CO_2]_2Cu$, forms beautiful blue crystals which dissolve in about 130 pts. of cold water. *Plumbic hydroxyacetate*, $[CH_2(OH).CO_2]_2Pb$, crystallizes in transparent monoclinic prisms soluble in about 30 pts. of cold water; in order to obtain this salt it is necessary to maintain the solution acid during concentration, otherwise a basic salt, $(C_2H_3O_3)_2OPb_2$, is produced (Fahlberg). *Ethylic hydroxyacetate*, $CH_2(OH).COOC_2H_5$, may be prepared by distilling a dry mixture of potassic hydroxyacetate and potassic ethylic sulphate from the oil bath, or by heating glycolide with alcohol at 200° (392° F.); it is a colourless liquid, which boils at 155° (311° F.). On treatment with phosphoric pentachloride it yields ethylic monochloracetate (Fahlberg; Norton and Tcherniak).

(1793) DEHYDROGLYCOLIC ACID and GLYCOLIDE.—If the syrup which remains on evaporating an aqueous solution of hydroxyacetic acid on the water-bath be further heated for any length of time it becomes incapable of crystallizing when exposed over sulphuric acid, and on pouring it into cold water only a portion dissolves, leaving a white insoluble residue of a compound formed by the withdrawal of the elements of a molecule of water from 2 mols. of hydroxyacetic acid, which, however, is more readily prepared by exposing the crystalline acid, together with sulphuric anhydride, under a bell jar for a few days, and washing the pulverulent product with cold water. This substance is insoluble in cold water, alcohol and ether, but dissolves in hot water, re-forming hydroxyacetic acid; by dissolving it in fused hydroxyacetic acid, a mixture is obtained which remains liquid on cooling; it melts at about 130° (266° F.), but if heated above this temperature, it gradually loses water and is converted into glycolide (Fahlberg, *loc. cit.*).

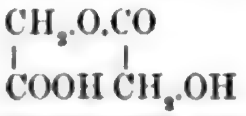
Glycolide is more readily prepared by gradually heating anhydrous sodic monochloracetate to a temperature of 150° (302° F.) for a couple of days, washing the product with warm water until the whole of the sodic chloride is removed, and drying the residue at 200° (392° F.) (Norton and Tcherniak, *Bull. Soc. Chem.*, xxx. 103). It is a white friable substance, melting at 220° (428° F.), insoluble, or nearly so, in most solvents; on boiling with water it is slowly dissolved and reconverted into hydroxyacetic acid, but ammonia readily attacks it, forming glycolamide, $CH_2(OH).CO.NH_2$, and amines have a similar action.

The following formulæ most probably represent the relation which these two compounds bear to hydroxyacetic acid (comp. 1802):



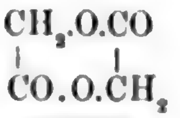
$$\begin{array}{l}CH_2.OH\\ |\\ COOH\end{array}$$

Glycolic acid.



$$\begin{array}{ll}CH_2.O.CO & \\ | & | \\ COOH & CH_2.OH\end{array}$$

Dehydroglycolic acid.



$$\begin{array}{l}CH_2.O.CO\\ |\qquad\quad |\\ CO.O.CH_2\end{array}$$

Glycolide.

(1794) DIGLYCOLIC ACID: $C_4H_6O_5 = O(CH_2.COOH)_2$.—When monochloracetic acid is heated with water, only glycolic acid is formed; but if a metallic oxide or hydrate be also present more or less diglycolic acid is usually produced. According to Schreiber (*Jour. pr. Chem.* [2], xiii. 436), the soluble metallic hydrates of the form M'.OH furnish chiefly glycolic acid, whereas, with those of the form M"(OH)$_2$, chiefly diglycolic acid is produced; lithic hydrate, however, behaves more like the hydrates of the alkaline-earthy metals, and magnesic oxide more like the hydrates of the alkali metals. With plumbic hydrate, both glycolic and diglycolic acids are formed; aluminic, zincic and stannous hydrates furnish only glycolic acid, the action taking place with remarkable slowness in the case of the last-mentioned hydrate; with the oxides of silver and mercury only glycolic acid is formed, but this partially undergoes oxidation to oxalic acid. The formation of diglycolic acid is doubtless due to the conversion of the glycolic acid first produced into a metallic derivative of the form $M'O.CH_2.COOM'$, which acts on the chloracetate simultaneously with the water, thus: $CH_2Cl.COOM + MO.CH_2.COOM = O(CH_2.COOM)_2 + MCl$.

Diglycolic acid may also be obtained by oxidizing diethylenic alcohol, $O(CH_2.CH_2.OH)_2$, with nitric acid (Wurtz). It crystallizes with 1 mol. of water in monoclinic prisms; the anhydrous acid melts at 148° (298°·4 F.). It furnishes a number of crystalline salts, which are mostly much less soluble than the corresponding glycolates.

(1795) ETHERIC ACIDS DERIVED FROM HYDROXYACETIC ACID.—By the action of the sodium derivatives of carbinols such as methylic, ethylic and amylic alcohol on chloracetic acid, Heintz has prepared a number of etheric acids of the form $CH_2(OC_nH_{2n+1}).COOH$; these compounds are not decomposed by alkalies, but when heated with hydriodic acid they exchange the C_nH_{2n+1} radicle for hydrogen.

(1796) THIOGLYCOLIC AND THIODIGLYCOLIC ACIDS.—These two acids are both produced on adding monochloracetic acid to a concentrated solution of potassic thiohydrate, KSH (Claesson, *Ann. Chem. Pharm.*, clxxxvii. 113); and their ethylic salts are formed in like manner from ethylic monochloracetate (Wislicenus, *ibid.*, cxlvi. 145). When neutralized with carbonates, hydrates or oxides of metals having less affinity for sulphur than for oxygen, thioglycolic acid furnishes normal salts of the form $CH_2(SH).COOM$; but metals having a greater affinity for sulphur than for oxygen displace the hydrogen in the SH group: thus, it is readily acted upon by mercuric oxide and converted into a compound of the formula $Hg\left\{\begin{array}{l}S.CH_2.COOH\\S.CH_2.COOH\end{array}\right.$, which crystallizes from hot water in long fine needles. On adding baric chloride and ammonia to a solution of the normal potassic salt, a white crystalline precipitate, almost insoluble in water, is produced, which has the composition represented by the formula

$$\left.\begin{array}{l}CH_2.S\\|\\COO\end{array}\right\}Ba \quad \text{or} \quad \begin{array}{l}CH_2.SBa.COO\\|\qquad\qquad\;\;|\\COO.BaS.CH_2\end{array}.$$

The selenium analogue of thiodiglycolic acid, $Se(CH_2.COOH)_2$, is obtained as ammonic salt by the action of ammonic monochloracetate on an alcoholic solution of ammonic selenide. It crystallizes from water in large colourless prisms (Schulze and Ulrich, *Deut. chem. Ges. Ber.*, viii. 773).

(1797) HYDROXYPROPIONIC OR LACTIC ACIDS: $C_3H_6O_3$.—Propionic acid theoretically can only furnish two monhydroxy-derivatives, viz.:

$CH_3.CH_2.COOH$	$CH_2(OH).CH_2.COOH$	$CH_3.CH(OH).COOH$
Propionic acid.	α-Hydroxypropionic acid.	β-Hydroxypropionic acid.

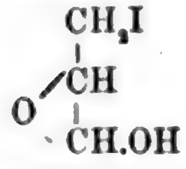
At least three distinct acids of the formula $C_3H_6O_3$ are known, however, but two of these appear merely to differ in certain physical properties and not in their general chemical behaviour.

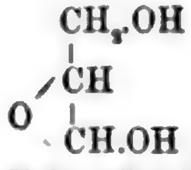
(1798) α-HYDROXYPROPIONIC ACID; *Ethylenelactic or Hydracrylic Acid*: $CH_2(OH).CH_2.COOH$.—This acid has been obtained 1. by displacing the iodine in α-iodopropionic acid (1769), $CH_2I.CH_2.COOH$, by the group OH by heating it with water in presence of metallic hydroxides, those of silver and calcium having been employed; 2. by heating α-cyanethylic alcohol (glycolic or ethylenic cyanhydrin), $CH_2(OH).CH_2.CN$, with water and an alkali or a mineral acid: $CH_2(OH).CH_2.CN + 2OH_2 = CH_2(OH).CH_2.COOH + NH_3$; and 3. as sodic salt by heating sodic acrylate with a solution of sodic hydrate at 100° (212° F.): $CH_2{=}CH.COONa + OH_2 = CH_2(OH).CH_2.COONa$.

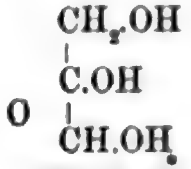
The action of argentic hydroxide on α-iodopropionic acid was first studied by Beilstein, who, however, assigned the formula $C_{12}H_{22}O_{11}$ to the acid produced, terming it *hydracrylic acid* on account of its conversion into acrylic acid and water on distillation. Two years later (1864) Moldenhauer published a paper in which he suggested that hydracrylic acid was merely an intermediate product, stating that it could be converted into an acid of the composition of lactic acid by heating its solution with alkalies, &c. Later on Wichelhaus, and subsequently Von Richter, endeavoured to prove that the lactic acid thus produced was sarcolactic acid, and not the ordinary acid obtainable by fermentation, but without obtaining very definite results. The true nature of the reaction was finally ascertained by Wislicenus, who showed that the iodopropionic acid was directly converted into an acid of the composition of lactic acid, but that, at the same time, acrylic acid, $C_3H_4O_2$, and two other isomeric acids of the composition $C_6H_{10}O_5$ (*dihydracrylic* and *paradipimalic acid*) were produced. The lactic acid thus prepared was reconverted with extreme readiness into α-iodopropionic acid by the action of hydriodic acid, and furnished crystalline salts.

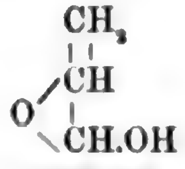
By digesting α-iodopropionic acid with milk of lime, Heintz also obtained acrylic and lactic acids, but did not observe the formation of an acid analogous to diglycolic acid (1794), or of the other acids obtained by Wislicenus (comp. *Ann. Chem. Pharm.*, clxvi. 6). In the course of his experiments Heintz discovered a comparatively difficultly soluble zinc-calcium double salt, highly characteristic of the lactic acid thus obtained, and this same salt was subsequently prepared by Wislicenus from the acid produced with the aid of argentic hydroxide.

By heating α-chlorethylic alcohol (glycolic or ethylenic chlorhydrin), $CH_2(OH).CH_2Cl$, with potassic cyanide and decomposing the resulting cyanhydrin, $CH_2(OH).CH_2.CN$, with alkali, Wislicenus had previously obtained an acid of the formula $C_3H_6O_3$ which appeared to be isomeric with that from iodopropionic acid, as it did not yield α-iodopropionic acid on treatment with hydriodic acid and gave only amorphous salts. From the manner in which it was formed, this acid was apparently the true "ethylenelactic" acid, $CH_2(OH).CH_2.COOH$, and in order to explain the isomerism between it and hydracrylic acid (this name being adopted for the lactic acid from α-iodopropionic acid), Wislicenus suggested that hydracrylic acid, α-iodopropionic acid, glyceric and acrylic acids were not, as was usually supposed, true carboxylic acids, but acids of peculiar constitution such as are represented by the following formulæ:


α-Iodopropionic acid


Hydracrylic acid.


Glyceric acid.


Acrylic acid.

Recent experiments of Erlenmeyer (*Ann. Chem. Pharm.*, cxci. 261) appear to show, however, that the conclusions drawn by Wislicenus were erroneous, for this chemist finds that the acid obtained from the chlorhydrin $CH_2(OH).CH_2Cl$ readily yields both α-iodopropionic acid and the zinc-calcium double salt characteristic of "hydracrylic acid." The amount of cyanhydrin, and therefore of acid, obtained from the chlorhydrin $CH_2(OH).CH_2Cl$ is very small. According to Erlenmeyer, a far better method of preparing the former consists in heating a mixture of ethylenic oxide and hydrocyanic acid in simple molecular proportions for several days at 50°—60° (122°—140° F.); the product is apparently a mixture of the cyanhydrin $CH_2(OH).CH_2.CN$ with a small quantity of the isomeric ethylidenic cyanhydrin (1630), $CH_3.CH(OH).CN$: it begins to boil at 190° (374° F.), but distils chiefly at about 220° (428° F.), the portion collected at the latter temperature consisting of the pure ethylenic cyanhydrin. When decomposed by boiling either with hydrochloric acid or with sodic hydrate solution, the pure α-cyanethylic alcohol yields both α-hydroxypropionic and acrylic acids together with a small amount of an amorphous nitrogenous compound.

According to Linnemann (*Deut. chem. Ges. Ber.*, viii. 1095), sodic acrylate is almost entirely converted into a mixture of the sodic salts of "hydracrylic" and Wislicenus's ethylenelactic acid by heating with an aqueous solution of sodic hydrate, the two salts being formed in about equal proportions; according to Erlenmeyer (*loc. cit.*), only α-hydroxypropionate is produced, much of the acrylate remaining unchanged.

In order to prepare pure α-hydroxypropionic acid from α-iodopropionic acid, the aqueous solution of the latter is digested with a slight excess of freshly precipitated argentic hydroxide, the dissolved silver is then removed by hydric sulphide, the solution neutralized with sodic carbonate, evaporated to dryness, and the residue extracted with boiling 95 per cent. alcohol; the salt which crystallizes out on cooling is purified by recrystallization from alcohol and may then be used for the preparation of the acid or of other salts.

α-Hydroxypropionic acid remains as a strongly acid syrup on evaporating its aqueous solution on the water-bath; when distilled, it is almost completely converted into acrylic acid and water, a decomposition which is still more readily effected by boiling it with a mixture of equal volumes of sulphuric acid and water. When oxidized with either chromic or nitric acid, it furnishes only oxalic acid besides carbonic acid; on boiling its solution with argentic oxide, carbonic anhydride is evolved from the commencement of the oxidation, and glycolic and oxalic acids are produced, carbacetoxylic acid being perhaps formed in the first instance; on fusing it with potassic hydrate, it yields chiefly formic and acetic acids, a little oxalic acid and perhaps glycolic acid being also formed. These results appear to indicate that the oxidation does not directly affect the $CH_2.OH$ group, but rather that the carboxyl group is the first to be attacked and split off.

Metallic α-Hydroxypropionates.—The *argentic* salt crystallizes in delicate needles and prisms, easily soluble even in cold water. *Sodic α-hydroxypropionate* is seldom obtained in distinct crystals, but usually separates from a hot alcoholic solution in crusts; it is difficultly soluble in hot anhydrous alcohol, but more soluble in 95 per cent. spirit; it is extremely deliquescent in moist air. The crystallized salt, after drying *in vacuo*, is anhydrous, and melts at about 143° (289°·4 F.) to a clear liquid; if heated to about 180° (356° F.), it slowly loses the elements of a molecule of water; the same change is rapidly effected if it be heated at 250° (482° F.). The product has the composition of sodic acrylate, but does not entirely consist of this salt, as it becomes warm on moistening with water, and may then be resolved into a mixture of sodic acrylate and of the sodic salts of the so-called dihydracrylic and paradipimalic acids (p. 885), the relation of which to the parent compound is not yet ascertained.

Calcic α-hydroxypropionate, $C_6H_{10}CaO_6 + 2OH_2$, although very soluble even in cold water, crystallizes in large, well-formed, apparently rhombic prisms. *Zincic α-hydroxypropionate*, $C_6H_{10}ZnO_6 + 4OH_2$, also crystallizes very readily in large triclinic prisms, soluble to the extent of 100 pts. in 119 pts. of water at 15°·5 (59°·9 F.), and miscible in all proportions with water heated above 60° (140° F.). The anhydrous salt melts at 160° (320° F.). On mixing concentrated solutions of the zinc and calcium salts in about equivalent proportions, a crystalline precipitate forms sooner or later, consisting of the double salt $C_6H_{10}CaO_6 . C_6H_{10}ZnO_6$; this salt dissolves in 11·5 pts. of water at 15° (59° F.) and is but slightly more soluble in hot water.

(1799) β-HYDROXYPROPIONIC OR METHHYDROXYACETIC ACID; *Ethylidenelactic Acid*: $CH_3.CH(OH).COOH$.—Two modifications of this acid are to be distinguished: the lactic acid produced by fermentation, which is the acid of sour milk, and sarcolactic acid which has hitherto only been obtained from flesh juice. The latter differs from the former in being optically active, and the salts derived from the two acids exhibit slight differences in composition; but they agree in their general chemical behaviour, and the active may be converted into the inactive acid. The nature of the isomerism which obtains between them cannot at present be explained.

(1800) INACTIVE β-HYDROXYPROPIONIC ACID; *Lactic Acid*.—Lactic acid or its salts may be obtained, 1. by heating β-chloro- or β-bromopropionic acid (1769) with water and metallic hydroxides; 2. by the action of nitrous acid on β-alanine (1775); 3. by exposing a concentrated solution of methylglycol, $CH_3.CH(OH).CH_2(OH)$, in contact with platinum-black to the air; 4. by digesting β-cyanethylic alcohol (1630) with hydrochloric acid; 5. by the action of nascent hydrogen on pyruvic acid, $CH_3.CO.COOH$; 6. by fusing glycerol with potassic hydrate (*ibid.* xi., 1167), or by boiling glyceric acid with a solution of potassic hydrate (Debus); 7. by heating dichloracetone, $CH_3.CO.CHCl_2$, with water at 200° (392° F.) (Linnemann and Zotta, *Ann. Chem. Pharm.*, clix. 247); 8. by heating glucose with a solution of sodic or baric hydrate (comp. p. 581), as much as 70—80 per cent. of the glucose being converted into the acid if the latter be employed (Schützenberger, *Deut. chem. Ges. Ber.*, ix. 448).

Lactic acid is best prepared by fermentation from cane sugar; as in the vinous fermentation, the sugar is first converted into glucoses, which are then resolved into two molecules of lactic acid: $C_6H_{12}O_6 = 2C_3H_6O_3$. This change takes place under the influence of a specific organism. The method usually adopted is to add a quantity of decayed cheese and sour milk, together with sufficient calcic or zincic carbonate to neutralize the acid as it forms, to a solution of sugar, and to set aside this mixture at a temperature of about 40°—45° (104°—113° F.) for eight or ten days. The cheese and milk simply serve as a means of introducing the organisms by which the decomposition is effected, and also supply the mineral salts and nitrogen necessary for the life and multiplication of these organisms; a much purer product would probably be as readily obtained if small quantities of the necessary mineral salts were dissolved in the sugar solution, and sufficient previously cultivated ferment then added to inoculate the liquid (comp. Fitz, *Deut. chem. Ges. Ber.*, xi. 1890).

Pure lactic acid of the formula $C_3H_6O_3$ cannot be obtained in consequence of the readiness with which it undergoes conversion into dehydrolactic acid, $C_6H_{10}O_5 = 2C_3H_6O_3 - OH_2$, this change taking place on mere exposure of a concentrated aqueous solution of the acid over sulphuric acid *in vacuo;* the strongly acid syrup obtained by evaporating a solution of the acid is probably a mixture of the compounds $CH_3.CH(OH).C(OH)_3$, $CH_3.CH(OH).COOH$, and $C_6H_{10}O_5$, and may even contain lactide, $C_6H_8O_4$ (Wislicenus, comp. 1802, 1803).

On distilling an aqueous solution of lactic acid, a certain amount of acid volatilizes with the steam; if the syrupy acid is slowly heated, lactide is produced, but if it be rapidly heated it is chiefly resolved into ethaldehyde, carbonic oxide and water: $CH_3.CH(OH).COOH = CH_3.COH + CO + OH_2$. Ethaldehyde is also produced together with formic acid on heating lactic acid with dilute sulphuric acid at 130° (266° F.): $CH_3.CH(OH).COOH + OH_2 = CH_3.CH(OH)_2 + H.COOH$: oxidizing agents such as a mixture of manganic dioxide and sulphuric acid act similarly, forming ethaldehyde and carbonic acid: $CH_3.CH(OH).COOH + (O + OH_2) = CH_3.CH(OH)_2 + HO.COOH$, but if more powerful oxidizing agents are employed acetic acid is produced. When fused with potassic hydrate it yields a certain amount of butyric acid (Hoppe-Seyler, *Zeits. physiolog. Chem.* 2, 14).

Lactic acid is converted into β-bromopropionic acid, $CH_3.CH(Br).COOH$, when heated with a saturated solution of hydrobromic acid at 100° (212° F.); when treated in a similar manner with hydriodic acid, however, it yields propionic acid, but β-iodopropionic acid is doubtless formed as an intermediate product. This iodo-acid may be obtained by acting on syrupy lactic acid with phosphorous iodide and treating the product with water. Phosphoric pentachloride readily acts on lactic acid and metallic lactates, forming β-chloropropionic chloride.

Lactic acid is itself capable of undergoing fermentation, and if in the preparation of the acid from sugar the fermentation be not stopped when the conversion into lactate is complete, the lactate gradually disappears, giving place to a mixture of acetate, normal butyrate and normal caproate. It may also be converted into propionic acid by fermentation (Fitz, *loc. cit.*).

Metallic lactates.—The salts of β-hydroxypropionic acid are less characteristic than those of the α-acid. The *calcic* salt, $C_6H_{10}CaO_6 + 5OH_2$, forms aggregates of small thin needles, soluble in 9—10 pts. of cold water. *Zincic* lactate, $C_6H_{10}ZnO_6 + 3OH_2$, crystallizes in small colourless prisms, soluble in about 60 pts. of cold water and in about 6 pts. of boiling water. *Sodic lactate* crystallizes only with difficulty and from very concentrated solutions; on adding sodium to the fused salt, hydrogen is evolved, so-called *disodic lactate* or *sodic sodoxypropionate*, $CH_3.CH(ONa).COONa$, being produced; this salt is immediately decomposed by water into sodic lactate and sodic hydrate.

Ethylic lactate, $CH_3.CH(OH).COOC_2H_5$, obtained by heating syrupy lactic acid with alcohol at 170° (338° F.), or by distilling a mixture of a metallic lactate and potassic ethylic sulphate, is a colourless liquid boiling at 156° (312°·8 F.); it is easily soluble in water, but the solution soon becomes acid from its decomposition into lactic acid and alcohol. Sodium dissolves in it with evolution of hydrogen, forming the compound $CH_3.CH(ONa).COOC_2H_5$, which, like disodic lactate, is immediately decomposed by water. Ethylic lactate is readily acted upon by the chlorides of phosphorus, but apparently two reactions occur simultaneously, a part being converted into ethylic chloropropionate by the simple displacement of the OH group by chlorine, while another part forms a complex phosphate, perhaps of the kind indicated by the equation:

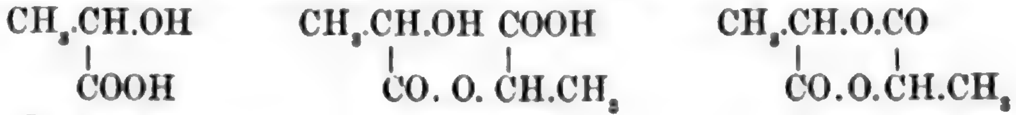
$$3HO.CH(CH_3).COOC_2H_5 + PCl_3 = 3HCl + P[O.CH(CH_3).COOC_2H_5]_3.$$

(1801) ETHERIC ACIDS DERIVED FROM LACTIC ACID.—By acting on ethylic sodoxypropionate with ethylic iodide, it is converted into *diethylic lactate* or *ethylic β-ethoxypropionate*, $CH_3.CH(OC_2H_5).COOC_2H_5$, which may also be obtained by the action of sodic ethylate on ethylic β-chloropropionate. Ethylic β-ethoxypropionate is a colourless liquid, boiling at about 156° (312° F.); it is insoluble in water. By boiling with potassic hydrate solution it is transformed into *potassic β-ethoxypropionate* and alcohol. The β-ethoxypropionic (ethyllactic) acid obtained from this salt is a somewhat viscid liquid which boils at about 195°—198° (383°—388°·4 F.), undergoing partial decomposition; it is not decomposed by alkalies, but when heated with concentrated hydriodic acid it yields lactic acid and ethylic iodide.

Similarly, ethylic lactate is converted by the action of acetic chloride into ethylic acetolactate or β-acetoxypropionate, $CH_3.CH(O.C_2H_3O).COOH$; and by heating this compound with twice its volume of water for two or three hours at 150° (302° F.), β-acetoxypropionic (acetolactic) acid is produced. The former is a colourless mobile neutral liquid, insoluble in water, boiling at 177° (350°·6 F.). The latter is a viscid, strongly acid liquid, which partially decomposes on distillation, and is easily soluble in water; when heated with water, it is gradually converted into acetic and lactic acids (comp. Wislicenus, *Ann. Chem. Pharm.*, cxxv. 49).

If lactic acid be dissolved in a mixture of concentrated nitric and sulphuric acids, and the solution be then poured into a large quantity of cold water, a colourless viscid heavy oil is obtained consisting of *β-nitroxypropionic* acid, $CH_3.CH(O.O_2N).COOH$. The ethylic salt of this acid is produced on heating ethylic lactate with a mixture of nitric and sulphuric acids; it is a colourless mobile liquid, having a strong odour like that of ethylic nitrate, boiling without decomposition at 178° (352°·4 F.) (Henry, *Deut. chem. Ges. Ber.*, iii. 532).

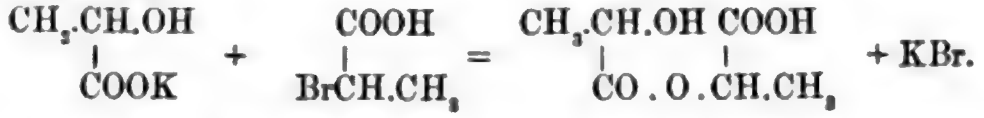
(1802) **Dehydrolactic Acid and Lactide.**—Lactic acid, as already mentioned, very readily loses a part of its hydrogen and oxygen as water, and thus gives rise to the formation of two compounds derived from 2 mols. of the acid by the withdrawal of the elements of 1 and 2 mols. of water respectively. The first of these—*dehydrolactic acid*, is a body of very complex functions, being at the same time monobasic acid, monohydric alcohol and ethereal salt; the second, *lactide*, is a perfectly neutral substance, and may be regarded as an ethereal salt of peculiar constitution. The relation of lactic acid to these two compounds will be evident on inspection of the following formulæ:



$$\begin{array}{l} CH_3.CH.OH \\ \quad | \\ \quad COOH \end{array} \qquad \begin{array}{l} CH_3.CH.OH\ COOH \\ \qquad | \qquad\quad | \\ \qquad CO.\ O.\ CH.CH_3 \end{array} \qquad \begin{array}{l} CH_3.CH.O.CO \\ \qquad | \qquad | \\ \quad CO.O.CH.CH_3 \end{array}$$

Lactic acid. Dehydrolactic acid.* Lactide.

Dehydrolactic acid is also formed on heating a mixture of potassic lactate and β-bromopionic acid at 100°—120° (212°—248° F.) (Van der Brüggen, *Zeits. Chem.* [2], v. 338):



$$\begin{array}{l} CH_3.CH.OH \\ \quad | \\ \quad COOK \end{array} + \begin{array}{l} \quad COOH \\ \quad | \\ BrCH.CH_3 \end{array} = \begin{array}{l} CH_3.CH.OH\ COOH \\ \quad | \qquad\quad | \\ CO\ .\ O\ .\ CH.CH_3 \end{array} + KBr.$$

The dehydration of lactic acid takes place even at ordinary temperatures on exposing an aqueous solution in a dry atmosphere, and still more rapidly at higher temperatures, dehydrolactic acid being produced in considerable quantity before the whole of the water is removed. The dehydro-acid and lactide are both reconverted into lactic acid by boiling with water; therefore it is possible to ascertain the composition of mixtures of lactic and dehydrolactic acids, or of the latter and lactide, by neutralizing the solution with normal alkali, then boiling with an excess of alkali, and afterwards determining the amount of alkali remaining unneutralized. In this manner Wislicenus (*Ann. Chem. Pharm.*, clxiv. 181) has analyzed the product obtained by gradual dehydration of an aqueous solution of lactic acid with the following results:

	Percentage composition.			
	Water.	Lactic acid.	Dehydrolactic acid.	Lactide.
1. Original aqueous acid; a thin syrup . .	15·64	58·80	25·56	—
2. After 4 months' exposure in the exsiccator; a syrupy liquid	4·07	22·43	73·50	—
3. After 13 months' exposure; a thick syrup, insoluble in water	—	—	97·85	2·06
4. After 16 months' exposure; a viscid syrup	—	—	71·41	28·69
5. After 18 months' exposure; a stiff mass, forming threads when drawn apart . .	—	—	60·77	39·50
1*a*. Original aqueous acid	26·23	69·59	4·18	—
2*a*. After heating for 8 hours on the water-bath in an open dish	—	44·93	55·11	—
3*a*. After 16 hours' ditto	—	30·00	71·49	—
4*a*. After heating the residue 3 for 15 hours at 140°—150° C. in a slow current of air	—	—	52·51	47·61

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* The name dilactic acid has been given to this compound, but this properly belongs to the dibasic acid $O[CH(CH_3).COOH]_2$ analogous to diglycolic acid (1794), which has not yet been prepared, however (comp. Van der Brüggen, *Ann. Chem. Pharm.*, cxlviii. 224; Heintz, clvii. 296).

The numbers in this table do not in all cases properly represent the composition of the product, lactide doubtless being also present in the residues obtained in experiments 2*a* and 3*a*, for example; but no method is known of quantitatively analyzing a mixture of lactic and dehydrolactic acids with lactide.

Pure dehydrolactic acid cannot be prepared on account of the impossibility of obtaining it free from lactic acid and lactide. Judging from the behaviour of products such as that produced in experiment 3 of the above Table, it is an amorphous substance almost insoluble in water, in contact with which it is only very slowly converted into lactic acid; on dissolving it in alcohol, adding an alcoholic solution of potassic hydrate and then precipitating with ether, an amorphous precipitate consisting of the potassic salt $C_6H_9KO_5$ is produced; by the action of ammonia, it is converted into a mixture of lactamide and ammonic lactate (Wislicenus).

Lactide is best prepared by passing a current of dry air through syrupy lactic acid in a retort heated at 150° (302° F.); it gradually sublimes and collects in the neck of the retort, leaving but a very small residue. After repeated recrystallization from absolute alcohol, it is obtained in colourless rhombic plates, melting at 124°·5 (256°·1 F.) (Wislicenus, *ibid.*, clxvii. 319). It boils at 255° (491° F.). It is insoluble in water, which very slowly converts it into dehydrolactic and lactic acids; alkalies act much more rapidly. It absorbs ammonia gas, forming lactamide $CH_3.CH(OH).CO.NH_2$. Its vapour density at 185° (365° F.) in Hofmann's apparatus corresponds with the formula $C_6H_8O_4$ (Henry, *Deut. chem. Ges. Ber.*, vii. 753).

(1803) SARCOLACTIC ACID; *Paralactic acid.*—This acid is contained in the liquid expressed from the flesh of the mammalia, being most abundant after *rigor mortis* has set in, and is also present in fish-flesh, and in oxen and pig's bile. Hilger has stated that it is produced on fermenting inosite, but Vohl denies this (*ibid.*, ix. 984). The product from flesh, according to Wislicenus (*Ann. Chem. Pharm.*, clxvii. 302, 355), does not entirely consist of sarcolactic acid, but also contains a relatively small amount of an acid identical with the so-called ethylenelactic acid he obtained from ethylenic cyanhydrin (comp. 1798); both Erlenmeyer and Klimenko, however, have failed in separating a second acid having the properties described by Wislicenus (*ibid.*, cxci. 266).

Sarcolactic acid is not distinguishable from ordinary (fermentation) lactic acid, except by its optical activity; but the zincic salts of the two acids differ greatly, for on slowly evaporating an aqueous solution the sarcolactate crystallizes out with only two molecules of water in well-formed, short, thick, glistening prisms, which are seldom united together; it is more soluble than the ordinary lactate, as it dissolves in 18·5 pts. of water at 14°—15° (57°·2—59° F.), and readily forms supersaturated solutions.

Sarcolactic acid, like ordinary lactic acid, is converted into ethaldehyde and formic acid when heated with dilute sulphuric acid at 130° (266° F.); and on oxidation with chromic acid, it yields a small quantity of ethaldehyde, together with acetic, formic and carbonic acids, but neither oxalic nor malonic acid* (Wislicenus).

By heating syrupy sarcolactic acid at 130°—140° (266°—284° F.), it is slowly converted into dehydro*lactic* acid, which yields the ordinary fermentation lactic acid when boiled with water (Strecker; Wislicenus); and by passing a current of dry air through the acid in a retort heated at 150° (302° F.), lactide is produced identical with that obtained from the inactive acid (Wislicenus). If a solution of sarcolactic acid be concentrated over sulphuric acid *in vacuo*, it also undergoes dehydration, but the resulting compounds exert a powerfully lœvorotatory action on polarized light (Wislicenus).

Optical Activity of Sarcolactic Acid and its Derivatives.—Wislicenus has shown that sarcolactic acid is a feebly dextrorotatory substance, but it is impossible to ascertain its exact rotatory power as it cannot be obtained in a pure state. The apparent specific rotatory power of the acid in an aqueous solution is immediately diminished by the addition of water, the diminution being the greater the more concentrated the solution; it afterwards gradually increases, but without attaining its original value.

The extent to which this takes place will be seen on inspection of the following Table:

	Amount of acid in 1 c.c. of solution.		$(\alpha)_D$.
Original solution, Oct. 24	·3994	...	2°·63
After dilution, Oct. 29	·3403	...	2°·01
Same solution, Nov. 7	·3407	...	2°·35
,, ,, Nov. 20	·3406	...	2°·26
,, ,, Nov. 30	·3406	...	2°·26
After further dilution, Dec. 4	·2124	...	1°·41
Same solution, Jan. 4	·2125	...	2°·07
,, ,, Feb. 12	·2125	...	2°·21
,, ,, March 12	·2125	...	2°·66
Again diluted, March 13	·1575	...	1°·99
Same solution, April 26	·1575	...	2°·29

To explain this behaviour, Wislicenus supposes that an aqueous solution of the acid contains not only the acid itself but also the corresponding "acid-hydrol," $C_3H_6O_3 + OH_2 = C_2H_4(OH).C(OH)_3$, and dehydro-acid, $C_6H_{10}O_5$. On adding water, a further quantity of the acidhydrol is immediately formed, and this having a lower specific rotatory power than the acid, the rotatory power is diminished; but the dehydro-acid, which is lœvorotatory, is also acted upon by the water, although much more slowly, and converted into the dextrorotatory acid, and therefore the dextrorotatory power gradually increases again.

Dehydrosarcolactic acid and sarcolactide are apparently both powerfully lævorotatory, a mixture consisting of 84·19 per cent. of the former with 16·04 per cent. of the latter in an alcoholic solution containing ·1954 gram per c.c., having the apparent sp. rot. power $(\alpha)_D = -85^{\circ}{\cdot}93$.

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* According to Dossios (*ibid.*, cxlvi. 168), crude sarcolactic acid yields malonic acid on oxidation, although in relatively very small quantity (Wislicenus, *ibid.*, clxvii. 335); but Erlenmeyer has attempted without success to confirm this statement.

The sarcolactates also are lævorotatory. Zincic sarcolactate, however, has a lower apparent sp. rot. power in supersaturated than in normal solution; thus the value of $(\alpha)_D$ for the salt $ZnC_6H_{10}O_6 + 2OH_2$ in the case of a solution containing 1 pt. of the salt to 86 pts. of water is – 6°·36, but – 7°·6 in the case of a solution containing 1 pt. of the salt to 18·5 pts. of water. The app. sp. rot. power of calcic sarcolactate calculated for the anhydrous salt in a solution containing ·0535 gram per c.c. is – 5°·25.

(1804) TRICHLOROLACTIC ACID: $C_3Cl_3H_3O_3 = CCl_3.CH(OH).COOH$.—The formation of this compound from trichlorethaldehydrol has already been described (p. 744). It crystallizes in prisms, melting at 105°—110° (221°—230° F.). It does not furnish characteristic metallic salts, but the ethylic salt crystallizes well from dilute alcohol in white needles, melting at 67° (152°·6 F.), and it boils at 233°—237° (451°·4—458°·6 F.). Alkalies readily decompose it into formate and trichlorethaldehydrol: $CCl_3.CH(OH).COOH + OH_2 = CCl_3.CH(OH)_2 + H.COOH$; the ethylic salt yields ethylic monochloracrylate when submitted to the action of nascent hydrogen, ethylic monochlorolactate probably being first produced: $CCl_3.CH(OH).COOC_2H_5 + 2H_2 = 2HCl + CH_2Cl.CH(OH).COOC_2H_5 = CHCl{=}CH.COOC_2H_5 + OH_2$. By heating with acetic anhydride, trichlorolactic acid is converted into the acetyl derivative $CCl_3.CH(O.C_2H_3O).COOH$, which separates from its solution in benzene in magnificent crystals, melting at 65° (149° F.) (Pinner and Fuchs, *Deut. chem. Ges. Ber.*, x. 1061).

By digesting bromal (p. 747) with hydrocyanic and hydrochloric acids, it is converted into *tribromolactic* acid, $CBr_3.CH(OH).COOH$, a crystalline compound melting at about 142° (287°·6 F.) (Pinner; Wallach, *Ann. Chem. Pharm.*, cxciii. 50).

(1805). CHLORALIDE AND ANALOGOUS COMPOUNDS.—The relation of chloralide to trichlorolactic acid, the methods of preparing it and its properties have previously been described (p. 744). The explanation which Wallach has given of its formation from chloral by the action of sulphuric acid involves the assumption that trichlorolactide is first produced; but it appears possible that, as Städler has suggested (*ibid.*, cvi. 253), it is derived from so-called metachloral, which perhaps is the polymeride of chloral corresponding to paraldehyde (1646). It is also probable that the carbonic oxide which is evolved is a direct product of the action, and that it is does not result from the decomposition of trichloromethane in the manner suggested by Wallach, as sulphuric acid does not act so readily on trichloromethane that the presence of the latter could be altogether overlooked if it were formed. A simple explanation of its production is afforded by the assumption that the group $CCl_3.CH$ is converted by the action of the sulphuric acid into the group $COCl.CH$, either by the direct displacement of two atoms of chlorine by one of oxygen, or by the formation first of an hydroxy-compound

$CCl_2(OH).CH$, which subsequently loses HCl, and that carbonic oxide and hydrochloric acid are then split off.

Wallach has shown that a large number of bodies analogous in composition to chloralide, and having similar properties, may be produced by the action of aldehydes such as trichlorethaldehyde, tribromethaldehyde and trichlorotetraldehyde (1632) on various hydroxy-acids, but that aldehydes such as ethaldehyde and benzaldehyde do not enter into reaction with hydroxy-acids under the conditions which furnish "chloralides;" it would therefore appear that only those aldehydes in which the radicle associated with the COH group is powerfully negative are available for the preparation of these compounds (*Ann. Chem. Pharm.*, cxciii. 1). The following may here be mentioned:

Glycolic chloralide, $CH_2\left\{\begin{matrix}O\\COO\end{matrix}\right\}CHCl_3$, prepared by heating a mixture of glycolic acid and chloral at 120°—130° (248°—256° F.), form small transparent crystals melting at 42° (107°·6 F.).

Lactic chloralide, $CH_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.CCl_3$, obtained by heating syrupy lactic acid with an excess of chloral at 150°—160° (302°—320° F.), closely resembles "chloralide" in appearance; it melts at 45° (113° F.), and boils unchanged at about 224° (435°·2 F.); chlorine has but little action upon it.

Bromalide, $CBr_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.CBr_3$, produced by heating a mixture of tribromolactic acid and bromal at 110°—120° (230°—248° F.), melts at 158° (316°·4 F.); it is rapidly decomposed by alcohol.

By heating a mixture of lactic acid and bromal, a bromalide of the formula $CH_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.CBr_3$ is obtained, which is also formed by the action of bromine on lactic acid in presence of alcohol (Klimenko, *Jour. pr. Chem.* [2], xiii. 98); it melts at 94°—97° (201°·2—206°·6 F.).

Isomeric compounds represented by the formulæ

$$CCl_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.CBr_3 \text{ and } CBr_3.CH\left\{\begin{matrix}O\\COO\end{matrix}\right\}CH.Cl_3$$

are respectively produced on heating mixtures of trichlorolactic acid and bromal and of tribromolactic acid and chloral; the former melts at about 150° (302° F.), and the latter at 132°—135° (269°·6—275° F.).

(1806) HYDROXYBUTYRIC ACIDS: $C_4H_8O_3=C_3H_6(OH).COOH$.—Of the five possible hydroxybutyric acids, the three which can be formed from normal butyric acid and one derived from isobutyric acid are known.

a-Hydroxybutyric acid, $CH_2(OH).CH_2.CH_2.COOH$, has been prepared by the action of baric hydrate on succinic aldehyde (1668), but not yet sufficiently examined. On oxidation it yields succinic acid; hydriodic acid appears to act upon it with difficulty.

β-Hydroxybutyric acid, $CH_3.CH(OH).CH_2.COOH$, may be obtained by oxidation of tetraldol (1631); by heating the compound $CH_3.CH(OH).CH_2Cl$ with potassic cyanide and decomposing the resulting cyanide by boiling with alkali (Markownikoff, *Ann. Chem. Pharm.*, cliii. 235); and by the action of nascent hydrogen on ethylic acetoacetate, $CH_3.CO.CH_2.COOC_2H_5$ (Wislicenus, *ibid.*, cxlix. 205). It is best prepared by the last-mentioned method, by adding sodium-amalgam to an aqueous solution of the acetoacetate.

The free acid is a viscid syrup, which on distillation decomposes into water and crotonic or *a*-methacrylic acid, $CH_3.CH{=}CH.COOH$. Its sodic salt crystallizes from nearly anhydrous alcohol in flat prisms, which are extremely deliquescent; the silver salt forms slender needles; the zincic, calcic and plumbic salts are amorphous and extremely soluble.

γ-Hydroxybutyric acid: $CH_3.CH_2.CH(OH).COOH$.—This acid, which is usually termed the *a*-acid, is obtained by digesting the bromobutyric acid produced on heating butyric acid with bromine (1770), with water and a metallic hydrate. It crystallizes from a concentrated aqueous solution in fine needles, melting at 44° (111°·2 F.); it begins to boil at 225° (437° F.), but the thermometer gradually rises to 260° (500° F.), at which temperature the retort contains a viscid liquid insoluble in water; the distillate is also only partially soluble in water, and does not deposit crystals even when cooled to 0° (32° F.), but salts of the acid may be prepared from it: probably therefore a dehydro-acid is formed. Characteristic of this acid is the zincic salt, which is difficultly soluble even in hot water, and separates from it in nodular aggregates consisting of fine four-sided prisms of the composition $(C_4H_7O_3)_2Zn + 2OH_2$ (Markownikoff, *loc. cit.*).

Dimethhydroxyacetic acid; hydroxyisobutyric, dimethoxalic, butylolactic or acetonic acid: $(CH_3)_2.C(OH).COOH$.—This acid is best prepared by digesting an aqueous solution of dimethbromacetic or bromisobutyric acid with a slight excess of baric hydrate, &c.; it is also formed by oxidation of dimethacetic acid by potassic permanganate (R. Meyer, *Deut. chem. Ges. Ber.*, xi. 1787); by oxidation of the amyleneglycol $(CH_3)_2.C(OH).CH(CH_3).OH$ (Wurtz); by digesting acetone with hydrocyanic and hydrochloric acids (Städler); and by Frankland and Duppa's method by the action of zincic methide on ethylic oxalate (1783, 7) (comp. Markownikoff, *loc. cit*). It crystallizes in prisms resembling oxalic acid, which melt at 75°·7 (168°·3 F.); it volatilizes slowly at the ordinary temperature, and readily sublimes at 50° (122° F.), being deposited on a cool surface in magnificent prisms; it boils at about 212° (413°·6 F.), and distils unchanged (Frankland and Duppa). According to Markownikoff (*ibid.*, cxlvi. 341), only the pure dry acid sublimes, and the sublimed acid melts at 79° (174°·2 F.). On oxidation, dimethhydroxyacetic acid yields dimethylketone and carbonic acid: $(CH_3)_2C(OH).COOH + (O + OH_2) = HO.COOH + (CH_3)_2C(OH)_2 = (CH_3)_2CO + OH_2$. The dimethhydroxyacetates mostly crystallize well, the zincic salt being the most characteristic: it is difficultly soluble both in cold and hot water, and crystallizes in microscopic six-sided plates of the composition $(C_4H_7O_3)_2Zn + 2OH_2$. The baric salt crystallizes in brilliant needles; the argentic salt in stellate groups of nacreous scales.

By heating bromisobutyric acid with an alcoholic solution of potassic hydroxide, it is converted into the etheric acid, *dimethethoxyacetic acid*, $C(CH_3)_2(OC_2H_5).COOH$, corresponding to dimethhydroxyacetic acid; this acid furnishes easily soluble salts, which crystallize well (Hell and Waldbauer, *Deut. chem. Ges. Ber.*, x. 448).

(1807) **Hydroxy-pentylic or valeric Acids.**—Only three of the considerable number of possible monhydroxy-derivatives of the four isomeric valeric acids are at present known; one of these is formed from isoprimary valeric or isopropacetic acid, the other two are derived from secondary valeric or methethacetic acid.

Isoprophydroxyacetic acid, $(CH_3)_2CH.CH(OH).COOH$, has been prepared from the corresponding isopropylbromacetic (bromisovaleric) acid (Fittig and Clark; Schmidt and Sachtleben, *Ann. Chem. Pharm.*, cxciii. 106), and also by Frankland and Duppa's method from ethylic oxalate, isopropylic iodide and zinc (Markownikoff, *Zeits. Chem.* [2], vi. 516). It crystallizes in plates melting at 82° (179°·6 F.), easily soluble in water and alcohol; its salts do not crystallize well; on oxidation, it yields isobutyric and carbonic acids (Ley and Popoff); on distillation it partially passes over unchanged, and is partially converted into the corresponding lactide, (?) $C_{10}H_{20}O_6$: the latter crystallizes from alcohol in fine white needles, melting at 136° (276°·8 F.); it is scarcely altered by dilute alkaline solutions.

An acid isomeric with the foregoing is formed on oxidizing valeric acid (from fermentation amylic alcohol) with potassic permanganate; it is converted into the corresponding acid of the acrylic series by merely boiling it with dilute sulphuric acid (comp. Miller, *Deut. chem. Ges. Ber.*, xi. 1527). Supposing it to be derived from isoprimary valeric acid, this acid probably has the formula $(CH_3)_2C(OH).CH_2.COOH$ (comp. *ibid.*, xi. 2216).

Methethhydroxyacetic or *methethoxalic acid*: $C_2H_5.C(CH_3)(OH).COOH$, is formed as ethylic salt on heating a mixture of ethylic oxalate, methylic and ethylic iodide and zinc; it melts at 63° (145°·4 F.), and sublimes readily at 100° (212° F.), condensing in magnificent stellate groups upon a cold surface; it boils, with decomposition, at 190° (374° F.). The baric and argentic salts crystallize well (Frankland and Duppa).

γ-Methyl-β-hydroxybutyric acid: $CH_3.CH(OH).CH(CH_3).COOH$.—This acid is formed as sodic salt on treating a solution of ethylic acetomethacetate in aqueous alcohol with sodium amalgam: $CH_3.CO.CH(CH_3).COOC_2H_5 + 2H + NaOH = CH_3.CH(OH).CH(CH_3).COONa + C_2H_5OH$. It does not crystallize, and cannot be obtained in a pure anhydrous state, as it is gradually converted into a dehydro-acid on exposure over sulphuric acid; on distillation it is resolved into water and *αβ*-dimethacrylic acid $CH_3.CH{=}C(CH_3).COOH$. The argentic salt crystallizes in glistening plates, very difficultly soluble even in boiling water (Rohrbeck, *Ann. Chem. Pharm.*, clxxxviii. 29).

Trichlorhydroxyvaleric acid, (?) $CH_3.CCl_2.CHCl.CH(OH).COOH$, is obtained from trichlorobutyric aldehyde (1632), by combining it with hydrocyanic acid and digesting the resulting cyanide with hydrochloric acid. It is a crystalline body, melting at 140° (284° F.), easily soluble in alcohol and in water. It furnishes a number of characteristic derivatives (comp. Pinner, *Deut. chem. Ges. Ber.*, xi. 1488).

(1808) **Hydroxycaproic Acids**: $C_6H_{12}O_3 = C_5H_{10}(OH).COOH$.—Only three of these acids are known, two being derived from diethacetic acid.

Leucic acid: (?) $C_4H_9.CH(OH).COOH$.—By the action of nitrous acid, leucine (from horn; 1779) is converted into the corresponding hydroxycaproic acid; the acid thus obtained crystallizes in hard brittle prisms, melting at 73° (163°·4 F.). Its baric and zincic salts both crystallize in glistening nacreous scales, very much like leucine itself, difficulty soluble in water; the former is anhydrous, the latter has the composition $Zn(C_6H_{11}O_3)_2 + OH_2$. The cupric salt is very difficultly soluble even in hot water, but readily crystallizes from hot alcohol in voluminous, pale-blue glistening scales (Waage, *Ann. Chem. Pharm.*, cxviii. 295).

Diethhydroxyacetic or *diethoxalic acid:* $(C_2H_5)_2C(OH).COOH$.—The ethylic salt of this acid is formed on digesting a mixture of ethylic oxalate and iodide with zinc. The acid itself crystallizes from a pure aqueous solution in minute prismatic needles, but if the solution contain a small quantity of sulphuric acid magnificent large prisms are obtained; it melts at 74°·5 (166°·1 F.), and decomposes on distillation. Its baric salt is very soluble even in cold water; its cupric salt does not crystallize; its zincic salt crystallizes in nacreous scales soluble in about 300 pts. of water at 16° (60°·8 F.) (Frankland and Duppa; Geuther and Wackenroder, *Zeits. Chem.* [2], iii. 705).

γ-Ethyl-β-hydroxybutric acid, $CH_3.CH(OH).CH(C_2H_5).COOH$, obtained by reducing ethylic acetoethacetate, $CH_3.CO.CH(C_2H_5).COOC_2H_5$, &c., is a colourless syrup which becomes viscid on exposure over sulphuric acid in consequence of the formation of the corresponding dehydro-acid; on distillation, it is resolved into water and α-methyl-β-ethylacrylic acid, $CH_3.CH{=\!=}C(C_2H_5)\,COOH$. Its argentic salt is almost insoluble in cold water, but crystallizes from hot water in aggregates of colourless glistening plates; on boiling an aqueous solution of the cupric salt, a blue insoluble basic salt is precipitated (Waldschmidt, *Ann. Chem. Pharm.*, clxxxviii. 240).

(1809) HYDROXYHEPTYLIC ACIDS: $C_7H_{14}O_3$.—Only two of these are known.

Isoamylhydroxyacetic acid: $C_5H_{11}.CH(OH).COOH$.—By digesting a mixture of ethylic oxalate and amylic iodide (from fermentation amylic alcohol) with zinc, Frankland and Duppa obtained a mixture of three ethylic salts boiling respectively at about 203° (397°·4 F.), 225° (437° F.) and 262° (503°·6 F.): the first of these was proved to be the ethylic salt of isoamylhydroxyacetic or amylhydroxalic acid; the second they regard as the ethylic salt of the corresponding etheric acid, *isoamylethoxyacetic acid*, $C_5H_{11}.CH(OC_2H_5).COOH$; the third is ethylic diisoamylhydroxyacetate. It is somewhat difficult to account for the formation of the first of these compounds, unless it be supposed that ethylic diisoamylhydroxyacetate is first produced and then partly resolved into isoamylhydroxyacetate and amylene:

$$(C_5H_{11})_2.C(OH).COOC_2H_5 \;=\; C_5H_{10} \;+\; C_5H_{11}.CH(OH).COOC_2H_5,$$

or that a splitting off of amylene takes place at the moment of the action of the zinc compound. The formation of the ethoxy salt shows that, supposing the action to take place in the manner suggested on p. 875, the OC_nH_{2n+1} group of the oxalate may remain intact and only the CO group be affected. Markownikoff has observed the formation of the three corresponding isopropyl derivatives when a mixture of ethylic oxalate and isopropylic iodide is digested with zinc.

According to Frankland and Duppa, the action of zincic amylide on ethereal salts of oxalic acid is susceptible of yet a fourth modification, for if *amylic* oxalate be employed instead of ethylic oxalate, in addition to the amylic salts corresponding to the three ethylic salts above mentioned, amylic caproate, $C_5H_{11}.COOC_5H_{11}$, is also produced; in explanation of the formation of this compound, they suggest that the molecule of amylic oxalate divides into its two constituent groups of $COOC_5H_{11}$, which then unite with amyl to form amylic caproate :

$$\begin{matrix} CO.OC_5H_{11} \\ | \\ CO.OC_5H_{11} \end{matrix} + 2C_5H_{11} = 2C_5H_{11}.COOC_5H_{11}.$$

But it may also be suggested as being more probable that a portion of the amylic oxalate is converted into amylic carbonate : $(CO.OC_5H_{11})_2 = CO(OC_5H_{11})_2 + CO$, and that the caproate results from the action of the zinc compound on this salt ; thus :

$$CO\left\{\begin{matrix} OC_5H_{11} \\ OC_5H_{11} \end{matrix}\right. + Zn(C_5H_{11})_2 = CO\left\{\begin{matrix} C_5H_{11} \\ OC_5H_{11} \end{matrix}\right. + Zn\left\{\begin{matrix} C_5H_{11} \\ OC_5H_{11} \end{matrix}\right. .$$

Isoamylhydroxyacetic acid crystallizes from water, in which it is sparingly soluble, in nacreous scales fusing at 60°·5 (140°·9 F.). The baric salt crystallizes in large nacreous scales like paraffin, tolerably soluble in water ; the cupric salt is very sparingly soluble and crystallizes in minute light-blue scales. The acid having these properties was obtained by Frankland and Duppa from a zinc salt remaining after treating the product of the action of zinc on a mixture of ethylic oxalate and amylic iodide with water and distilling off the ethylic salts above mentioned ; the acid prepared from the ethylic salt boiling at 203° C. did not crystallize, and its baric salt was only obtained as a crystalline mass.

γ^2-*Metheth-β-hydroxybutyric acid*, $CH_3.CH(OH).C\left\{\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\right\}.COOH$, has been obtained by reduction of ethylic acetomethethacetate, but not yet examined : its argentic salt is moderately soluble in hot water, from which it crystallizes in glistening plates ; on adding cupric sulphate to a solution of its sodic salt and then boiling, a crystalline basic cupric salt is deposited.

(1810) Hydroxyoctylic Acids: $C_8H_{16}O_3 = C_7H_{14}(OH).COOH$.—Only two monhydroxy-derivatives of the very large number of possible octylic acids have been prepared.

Normal-hexylhydroxyacetic acid, $C_6H_{13}{}^{\alpha}.CH(OH).COOH$, is obtained by digesting the cyanoctylic alcohol produced by combining normal heptaldehyde with hydrocyanic acid with hydrochloric acid. It crystallizes in large nacreous scales, melting at 69°·5 (157°·1 F.), very difficultly soluble in water ; when heated with hydrochloric acid at 120° (248° F.), it yields formic acid and heptaldehyde (Erlenmeyer and Sigel, *Ann. Chem. Pharm.*, clxxvii. 102).

Diisopropylhydroxyacetic acid, $(C_3H_7)_2{}^{\beta}.CH(OH).COOH$, prepared by Frankland and Duppa's method, crystallizes in colourless slender needles, melting at 111° (231°·8 F.), difficultly soluble in cold water. It yields isopropyl ketone on oxidation (Markownikoff).

(1811) Hydroxydodecylic Acids: $C_{12}H_{24}O_3$.—Two of these acids, the highest terms of the series at present known, have been obtained.

Diisoamylhydroxyacetic acid, $(C_5H_{11})_2.CH(OH).COOH$ (comp. 1810), crystallizes in colourless satiny fibres, insoluble in water ; it melts at 122° (251°·6 F.), and when more strongly heated sublimes in white snow-like flakes (Frankland and Duppa).

γ^2-*Dieth-β-hydroxybutyric acid*, $CH_3.CH(OH).C(C_2H_5)_2.COOH$, prepared by reducing ethylic acetodiethacetate, does not crystallize, but gradually undergoes conversion into the corresponding dehydro-acid on exposure over sulphuric acid; on distillation it is resolved into ethaldehyde and diethacetic acid (Schnapp, *Deut. chem. Ges. Ber.*, ix. 1216).

DI-, TRI- AND PENTHYDROXY-ACIDS DERIVED FROM THE ACIDS OF THE ACETIC SERIES.

(1812) Only the following are known:

Dihydroxyacetic or glyoxylic acid	$CH(OH)_2.COOH$
α-β-Dihydroxypropionic or glyceric acid	$CH_2(OH).CH(OH).COOH$
Dihydroxybutyric acid	$C_3H_5(OH)_2.COOH$
α-β-γ-Trihydroxybutyric acid	$C_3H_4(OH)_3.COOH$
Penthydroxycaproic acids:	
Mannitic acid	$C_5H_6(OH)_5.COOH$
Gluconic "	
Dextronic "	

(1813) DIHYDROXYACETIC OR GLYOXYLIC ACID: $C_2H_4O_4 = CH(OH)_2.COOH$.—This acid was first discovered by Debus among the products of the oxidation of ethylic alcohol by dilute nitric acid, and was subsequently obtained by him in a similar manner from glycol and oxaldehyde or glyoxal; according to Heintz, it is a product of the oxidation of glycolic acid and of glycerol (p. 544). It is also formed on boiling the argentic salt of dibromacetic acid with water (Perkin and Duppa); and, according to Church, it may be obtained by the action of nascent hydrogen on oxalic acid.

Debus, who has denied the possibility of the existence of compounds containing more than a single hydroxyl-group associated with the same carbon atom, maintains that the acid thus produced is not dihydroxyacetic acid but the aldehyde-acid of the formula COH.COOH, and considers that this conclusion is supported by the facts (1) that it is formed from the aldehyde $C_2H_2O_2$, and that the acids contain the same number of hydrogen atoms as the aldehyde from which they are derived; (2) that it exhibits certain of the properties of aldehydes, combining, for example, with acid sulphites; and (3) that it furnishes an ammonic salt of the formula $C_2HO_3(NH_4)$. It has already been pointed out, however (1491), that the behaviour of aldehydes such as meth- and ethaldehyde necessitates the conclusion that compounds containing more than a single OH group associated with the same carbon atom can and do exist, and that in the formation of acetic acid from ethaldehyde, for example, the latter is probably first converted into ethaldehydrol, which is then oxidized and converted into the ortho-acid or acid-hydrol corresponding to acetic acid. Similarly, it may be supposed that an aqueous solution of oxaldehyde contains oxaldehydrol, $CH(OH)_2.CH(OH)_2$, and that this on oxidation yields the compound $CH(OH)_2.C(OH)_3$, which is subsequently resolved into dihydroxyacetic acid and water. The formation of the compounds with acid sulphites may be equally well explained by aid of either formula. The nature of the ammonic salt in question will be considered later on.

To prepare dihydroxyacetic acid from alcohol, 220 grams of 80 per cent.

spirit is placed in a tall narrow flask of about 1·5 litre capacity, and by means of a funnel-tube drawn out to a fine point 100 grams of water is carefully introduced below the alcohol, and afterwards 200 grams of red fuming nitric acid is poured in so as to form a layer below the water; the flask is closed with a cork provided with a bent tube dipping under water, and is then left at a temperature of 20°—22° (68°—71°·6 F.) until the three liquids have become completely mixed, which is usually the case after 6 or 8 days. This product is evaporated to a syrup on the water-bath in portions of not more than 20—30 grams, and the residues—consisting of glyoxal, glycolic, glyoxylic and oxalic acids—are dissolved in a small quantity of water, the solution is neutralized with calcic carbonate, about an equal volume of alcohol is then added and the whole thrown on a linen filter; finally, the residue on the filter, after being well pressed, is repeatedly extracted with boiling water. The solution thus obtained deposits calcic glyoxylate in hard prismatic crystals, or if sufficiently concentrated solidifies to a gelatinous mass of fine needles, which after a few days shrinks together in consequence of the formation of the prismatic crystals; a second and third crop of crystals may be obtained by concentrating the mother liquor. The free acid is prepared from the calcic salt by double decomposition with the equivalent amount of oxalic acid (Debus).

To procure dihydroxyacetic acid from dibromacetic acid, an aqueous solution of argentic dibromacetate is boiled until the whole of the silver is separated as argentic bromide: $2CHBr_2.COOAg + 2OH_2 = CH(OH)_2.COOH + CHBr_2.COOH + 2AgBr$; the resulting solution of dihydroxy- and dibromacetic acids is then carefully neutralized with argentic carbonate and boiled until argentic bromide ceases to be formed: $CH(OH)_2.COOAg + CHBr_2.COOAg + 2OH_2 = 2CH(OH)_2.COOH + 2AgBr$. The filtrate from the argentic bromide is evaporated to a small bulk on the water-bath, sufficient hydrochloric acid is then added to remove the traces of silver present, and the solution further concentrated over sulphuric acid, when it gradually solidifies to a mass of crystals (Perkin, *Journ. Chem. Soc.*, 1877, ii. 96).

Dihydroxyacetic acid crystallizes apparently in monoclinic prisms, very soluble in water and alcohol; when heated it melts to a syrupy liquid, which cannot be distilled without decomposition (Perkin). According to Debus, on distilling an aqueous solution of the acid, at first pure water and afterwards the unchanged acid pass over; and on heating the syrupy acid in a test-tube it volatilizes, leaving only a slight black residue. It is reduced to hydroxyacetic or glycolic acid by nascent hydrogen, zinc dissolving in it without evolution of hydrogen in consequence of this behaviour; it is scarcely affected, however, by hydriodic acid at 100° (212° F.) (Debus). Alkaline hydrates very readily act upon it, converting it half into the corresponding glycolate and half into oxalate, mere boiling of a solution of its calcic salt, for example, for a few seconds with a slight excess of lime-water or milk of lime being sufficient to completely decompose it in this manner; this reaction affords a ready means both of detecting and of estimating the acid, it being merely necessary in the latter case to ascertain the amount of oxalate precipitated. The reaction may be represented by the following equations, supposing the potassic salt and potassic hydrate to be employed:

$$\mathrm{CH(OH)_2.COOK + KOH = H + C(OK)(OH)_2.COOK = COOK.COOK + OH_2;}$$
$$\mathrm{CH(OH)_2.COOK + H = CH_2(OH).COOK + OH_2.}$$

Dihydroxyacetic acid is also converted into hydroxyacetic acid on adding hydrochloric acid to a mixture of the former and hydrocyanic acid, the reaction being attended with the evolution of carbonic anhydride (Böttinger, *Deut. chem. Ges. Ber.*, x. 1084).

On the other hand, it is very readily oxidized, and reduces an ammoniacal solution of a silver salt, forming a brilliant silver mirror. It is decomposed by hydric sulphide, but the nature of the reaction has not yet been satisfactorily ascertained (Debus; Böttinger, *ibid.*, x. 1243).

Dihydroxyacetates.—The metallic dihydroxyacetates all correspond in composition to the formula $C_2H_3M'O_4$, and cannot be deprived of the elements of water without undergoing decomposition; they are obtained by neutralizing the acid with metallic carbonates, or by double decomposition from the calcic salt.

Calcic Dihydroxyacetate, $[CH(OH)_2.COO]_2Ca$, crystallizes in hard prisms or thin needles, soluble in 177 pts. of water at 8° (46°·4 F.); it may be heated at 160°—170° (320°—338° F.) without loss of weight, but at 180° (356° F.) it is decomposed, water and carbonic anhydride being given off, leaving a residue consisting of calcic carbonate, glycolate and oxalate, together with a resinous substance. On adding lime-water to its solution, a white flocculent precipitate, apparently consisting of a basic salt, is produced; this gradually decomposes at ordinary temperatures and rapidly on heating, furnishing a mixture of calcic glycolate and oxalate.

On adding the equivalent quantity of ammonic oxalate to a solution of calcic dihydroxyacetate, and evaporating the filtered liquid *in vacuo*, crusts of prismatic crystals of the composition $C_2H_5NO_3$, are obtained. According to Perkin (*loc. cit.*), although the freshly prepared solution is neutral, it gradually becomes acid on evaporation, and he therefore infers that the ammonic dihydroxyacetate first produced is gradually converted into the compound $C_2H_5NO_3$, which may be regarded as amidohydroxyacetic acid, $CH(NH_2)(OH).COOH$, analogous to "aldehyde ammonia," but Debus points out that many other ammonic salts behave similarly when their aqueous solutions are evaporated, and that ammonia is at once evolved on treating the compound $C_2H_5NO_3$ with alkali, which is not the case with "aldehyde-ammonia." The existence of an ammonic salt of the formula $COH.COONH_4$, however, is no proof of the non-existence of an acid of the formula $CH(OH)_2.COOH$ and of salts derived from it, or of the existence of an acid of the formula $COH.COOH$; it merely tends to show that compounds of both forms are possible, corresponding to ethaldehydrol $CH_3.CH(OH)_2$, and ethaldehyde, $CH_3.COH$. If aniline oxalate be employed instead of ammonic oxalate, a clear solution is at first obtained, which, however, quickly changes and becomes yellow, depositing an orange-coloured powder; this product does not possess the properties of a salt, but is soluble in both ammonia and dilute hydrochloric acid. The compound $C_2H_5NO_3$ dissolves in large quantity in water; on boiling the solution, carbonic anhydride is evolved and a brown resinous substance produced. A number of the metallic dihydroxyacetates enter into reaction with ammonia (comp. Debus, *Ann. Chem. Pharm.*, cxxvi. 136)

Sodic and calcic dihydroxyacetates form compounds with the corresponding acid sulphites, apparently analagous to those obtained from the aldehydes:

$$CH(OH)_2.COONa + HNaSO_3 = CH(OH)(NaSO_3).COONa + OH_2.$$
$$CH(OH)_2.CH_3 + HNaSO_3 = CH(OH)(NaSO_3).CH_3 + OH_2.$$

By heating crystalline dihydroxyacetic acid with alcohol at 120°—130° (248°—266° F.), it is apparently converted into ethylic diethoxyacetate, $CH(OC_2H_5)_2.COOC_2H_5$ (Perkin), but this compound is more readily prepared from dichloracetic acid (Schreiber, *Zeits. Chem.* [2], vi. 167).

(1814) **α-β-DIHYDROXYPROPIONIC OR GLYCERIC ACID**: $C_3H_6O_4 = CH_2(OH).CH(OH).COOH$.—This acid is obtained by oxidizing glycerol, either with dilute nitric acid (Debus, Socoloff), or by heating it with bromine and water (Barth).

To prepare it, 100 pts. of glycerol dissolved in about an equal bulk of water is placed in a glass cylinder, and 100—125 pts. of fuming nitric acid is introduced below it by means of a funnel-tube. The two layers of liquid gradually mix, and gas is copiously evolved. After several days, when the oxidation is completed, the product is evaporated in a large flat dish on the water-bath; the syrupy residue is dissolved in a considerable quantity of water, the solution is then heated to boiling, neutralized with plumbic carbonate or oxide, care being taken to avoid an excess if the latter be employed, and is filtered while still hot; as the liquid cools, crude plumbic glycerate is deposited in crystalline crusts. It is purified by *repeated* recrystallization, with the aid of animal charcoal. To obtain the free acid, a warm saturated solution of the plumbic salt is decomposed with hydric sulphide (comp. Mulder, *Deut. chem. Ges. Ber.*, ix. 1902).

Glyceric acid forms a colourless thick syrup, soluble in all proportions in water and alcohol. Its metallic salts are soluble in water and mostly crystallize well; they all correspond in composition with the formula $C_3H_5M'O_4$. It appears to behave like lactic acid when heated: that is to say, it loses the elements of water and yields dehydro-derivatives; when distilled, it yields pyruvic acid, $CH_3.CO.COOH$. It is readily converted into α-iodopropionic acid by the action of phosphorus iodide or hydriodic acid, 90 per cent. of the theoretical amount of iodo-acid being obtainable (comp. Erlenmeyer, *Ann. Chem. Pharm.*, cxci. 284). It yields the corresponding α-chloropropionic acid when submitted to the action of phosphoric pentachloride (Wichelhaus; Heintz, *ibid.*, clvi. 35); the amount produced is small, however, and the nature of the reaction by which it is formed is at present obscure. Glyceric acid is very readily oxidized; it reduces an ammoniacal solution of a silver salt. It is much more stable than dihydroxyacetic acid in presence of alkaline hydrates, a solution of baric glycerate being unaffected by several hours' boiling with baric hydrate (Debus); but on boiling down with potassic hydrate, it yields a mixture of potassic lactate, formate and oxalate (Debus), the first of these products resulting doubtless from the action of the hydrogen displaced in the formation of the two latter.

(1815) β^2-DIHYDROXYPROPIONIC ACID: $CH_3.C(OH)_2.COOH$.—This acid is not known in the free state, but probably is a constituent of an aqueous solution of acetoformic acid (1820). The trichloro-derivative, so-called *isotrichloroglyceric acid*, $CCl_3.C(OH)_2.COOH$, is produced on treating gallic and salicylic acid or phenol with a mixture of potassic chlorate and hydrochloric acid. It crystallizes in long flat needles, melting at about 100° (212° F.), extremely soluble in all ordinary solvents; it readily sublimes, and may even be distilled without much loss. It is at once decomposed by alkalies, forming trichloromethane and an oxalate: $CCl_3.C(OH)_2.COOH + OH_2 = CCl_3H + C(OH)_3.COOH = COOH.COOH + OH_2$; and nascent hydrogen converts it into lactic acid (Schreder, *Ann. Chem. Pharm.*, clxxvii. 282).

The tribromo-acid obtained by Grimaux (*Compt. Rend.*, lxxviii. 974) by the action of bromine on acetoformic and lactic acids has very similar properties; it crystallizes in naphthalene-like plates of the composition $C_3HBr_3O_3 + 2OH_2 = (?)$ $CBr_3.C(OH)_2.C(OH)_2$, which are not altered on exposure *in vacuo*, but only lose their (?) water of crystallization after several hours' heating at 100° (212° F.).

A closely allied compound, which probably has the formula $CBr_3.C(NO_2)_2.COOH$, is produced on treating tribromophloroglucol (1535) with nitric acid; this body yields nitrotribromomethane and oxalic acid on decomposition by water (Benedikt, *Ann. Chem. Pharm.*, clxxxiv. 255).

(1816) TRIHYDROXYBUTYRIC ACID: $C_4H_8O_5 = C_3H_4(OH)_3.COOH$.—The acid obtained by oxidation of erythrol (1540) probably has this constitution. Little is known of its properties (comp. Sell, *Compt. Rend.*, lxi. 741; Lamparter, *Ann. Chem. Pharm.*, cxxxiv. 260).

(1817) PENTHYDROXYCAPROIC ACIDS: $C_6H_{12}O_7 = C_5H_6(OH)_5.COOH$.—Three acids which may be regarded as having this constitution are known, viz., mannitic, gluconic and dextronic acids.

Mannitic acid, obtained by oxidation of mannitol (1545), is an amorphous extremely soluble substance. The metallic salts which have been prepared from it are amorphous and mostly very soluble, but they are apparently basic salts (Gorup-Besanez, *ibid.*, cxviii. 257).

Gluconic and dextronic acids.—The formation of these acids from dextroglucose and starch respectively has already been described (pp. 582, 625): the latter may also be obtained from dextrin (Habermann, *Ann. Chem. Pharm.*, clxii. 297). Both are optically active, but dextronic acid has a slightly higher dextrorotatory power than gluconic acid. Their baric and calcic salts also differ slightly in composition, that of the gluconates being represented by the formulæ $(C_6H_{11}O_7)_2Ba + 3OH_2$ and $(C_6H_{11}O_7)_2Ca + 2OH_2$, the dextronates by the formulæ $(C_6H_{11}O_7)_2Ba + 4OH_2$ and $(C_6H_{11}O_7)_2Ca + OH_2$, but, according to Habermann, baric dextronate is converted into the isomeric gluconate on recrystallization.

ACIDS OF THE FORM $C_nH_{2n-1}O.COOH$ DERIVED FROM THE ACIDS OF THE ACETIC SERIES.

KETONIC ACIDS OF THE ACETOFORMIC SERIES.

(1818) The acids of this form may be regarded as derived from the acids of the acetic series by the displacement of two atoms of hydrogen in the C_nH_{2n+1} radicle by a single atom of oxygen; the acids produced when both the atoms of hydrogen which are displaced are associated with the same carbon atom may be represented by the general formula $C_mH_{2m+1}.CO.C_nH_{2n}.COOH$, whereas those formed by the displacement of hydrogen atoms associated with contiguous carbon atoms may be regarded as derivatives of ethylenic oxide and its homologues. Only one representative of this latter class is known, but the former includes a considerable number of acids. The monhydroxy-derivatives of the acids of the acrylic series would also be acids of the form $CNH_{2n-1}O.COOH$, but at the present such are not known with certainty to exist (comp. Ricinoleic Acid).

The acids of the form $C_mH_{2m+1}.CO.C_nH_{2n}.COOH$ may be termed *ketonic acids*, as in consequence of the presence of the group CO they exhibit many of the reactions characteristic of ketones in addition to the ordinary reactions of acids. An acid of this form obviously cannot be derived from formic acid. The acid of the formula COH.COOH, derived from acetic acid, is theoretically the first term of the series, but there is no satisfactory evidence of the existence of such a compound (comp. p. 901), the lowest term of the series being acetoformic or pyruvic acid, $CH_3.CO.COOH$, which is derived from propionic acid.

Obviously the acids of the form $C_nH_{2n-1}O.COOH$ may equally well be regarded as derived from the monhydroxy-derivatives of the acids of the acetic series by the withdrawal of two atoms of hydrogen, or from the dihydroxy-acids by the removal of the elements of a molecule of water.

The ketonic acids are conveniently distinguished by regarding them as formed by the introduction of so-called acid radicles of the form $C_nH_{2n+1}.CO$ in place of an atom of hydrogen in the C_nH_{2n+1} radicle of the acids of the acetic series; thus pyruvic acid is acetoformic acid, and the compound $CH_3.CO.CH_2.COOH$ acetoacetic acid.

The ketonic acids cannot all exist in the free state or as metallic salts, some being only known as ethereal salts; this apparently is the case with all acids of the forms $R.CO.CH_2.COOH$, $R.CO.CHR.COOH$ and $R.CO.C(R_2).COOH$.

(1819) Acetoformic Acid; *Pyruvic* or *Pyroracemic acid:* $C_3H_4O_3 = CH_3.CO.COOH$.—This acid was discovered by Berzelius in 1830, who obtained it as a product of the dry distillation of tartaric acid. It is also formed by dry distillation of glyceric acid (Moldenhauer; comp. Böttinger, *Deut. chem. Ges. Ber.*, x. 266). It may be produced synthetically—1. by heating β^2-dichloropropionic acid (1769) with water alone, or with water and a metallic hydroxide or carbonate; 2. by heating argentic chloracrylate with water: $CH_2{=}CCl.COOAg + OH_2 = CH_3.CCl(OH).COOAg = CH_3.CO.COOAg + HCl = CH_3.CO.COOH + AgCl$ (Beckurts and Otto, *ibid.*, x. 265, 2037); and 3. by warming acetoformamide, $CH_3.CO.CO.NH_2$, with a slight excess of dilute hydrochloric acid (1757; comp. *ibid.*, xi. 1563).

As obtained by rectifying the crude distillate from tartaric acid several times, collecting apart the portion which boils at 155°—165° (311°—329° F.), acetoformic acid is a somewhat viscid liquid of the sp. gr. 1°·24—1°·26, readily soluble in water and alcohol. If it be heated at about 170° (338° F.) for several hours, carbonic anhydride is evolved, and it is converted into a resinous mass, from which hot water extracts small quantities of acetic, pyrotartaric and uvic acids (Böttinger, *Ann. Chem. Pharm.*, clxxxviii. 293); and as this decomposition also takes place to a certain extent on mere distillation of the acid, it cannot be obtained of fixed boiling point. By the action of sodium amalgam on its aqueous solution, or by heating with hydriodic acid, it is converted into lactic acid (Wislicenus), which is also produced by dissolving zinc in a mixture of acetoformic and acetic acids (Debus); if an alcoholic solution be digested with zinc, a small quantity of dimethyltartaric acid is also formed: $2CH_3.CO.COOH + 2H = [CH_3.C(OH).COOH]_2$ (Böttinger). Another method of converting it into lactic acid consists in digesting it with hydrocyanic acid and warming the product with hydrochloric acid (Böttinger). On oxidation, acetoformic acid yields either carbonic and acetic, or carbonic and oxalic acid, according to the nature of the oxidizing agent.

It combines directly with bromine, forming an extremely unstable crystalline dibromide, $C_3H_4Br_2O_3$, which appears to be converted into a crystalline monobromopyruvic acid by the action of water (Wislicenus, *ibid.*, cxlviii. 208). By heating pyruvic acid dissolved in a small quantity of water with a single molecular proportion of bromine until the latter disappears, a liquid monobromo-acid is obtained; if twice the quantity of bromine be taken, a crystalline dibromo-acid, $C_3H_2Br_2O_3 + 2OH_2 = (?)\ CHBr_2.C(OH)_2.C(OH)_3$, is formed; but if the heating be continued after the bromine is absorbed, the hydrobromic acid present acts upon this dibromo-acid, converting it into pentabromacetone: $CHBr_2.C(OH)_2.COOH + 3HBr = CHBr_2.CO\ CBr_3 + 3OH_2$ (Wichelhaus, *ibid.*, clii. 260). By employing a still larger amount of bromine, a crystalline tribromo-derivative is produced (comp. 1814). On treatment with phosphoric pentachloride, pyruvic acid yields β^2-dichloropropionic chloride, $CH_3\ CCl_2.COCl$ (Klimenko).

By passing hydric sulphide into the freshly distilled acid it is converted into a white pulverulent substance of the formula $C_6H_{10}SO_5$; by the action of hydriodic acid this product is transformed into crystalline β-thiohydropropionic acid, $CH_3.CH(SH).COOH$, identical with that obtained from β-chloropropionic acid and a metallic thiohydrate; this latter compound is also produced on saturating a solution of argentic acetoformate with hydric sulphide (Böttinger).

Pyruvic acid gradually alters when kept, becoming yellow-coloured and viscid, and it cannot be recovered entirely unchanged from its salts; if it be several times evaporated with water on the water-bath, it is almost completely converted into a syrupy acid, incapable of forming crystalline salts, which apparently is a polymeric modification of the original acid. It also undergoes condensation with remarkable facility, yielding pyrotartaric acid, $C_5H_8O_4$. and mesaconic acid, $C_5H_6O_4$, on digestion with hydrochloric acid; and uvic, $C_7H_8O_3$, and a dimethylbenzoic acid (uvitic acid), $C_9H_8O_2$, together with acetic and oxalic acid and other products, on boiling its aqueous solution with baric hydrate (comp. Böttinger, *loc. cit.*; *ibid.*, clxxii. 239).

Metallic acetoformates.—The most characteristic salt is the argentic salt, $CH_3.CO.COOAg$, obtained by neutralizing a warm solution of the acid with argentic carbonate; it crystallizes in broad plates and prisms. The baric, potassic, and sodic salts are also crystalline, provided that they are prepared without the aid of heat, but if their solutions are concentrated on the water-bath they form gummy amorphous masses. On adding an excess of baric hydrate solution to a solution of pyruvic acid, a white precipitate is produced, to which Finck assigns the somewhat improbable formula $C_{18}H_{18}Ba_3O_{18}.BaH_2O_2$.

(1820) **Hydroxyacetoformic Acid or Carbacetoxylic Acid**: $C_3H_4O_4 = CH_2(OH).CO.COOH$.—According to Wichelhaus (*ibid.*, cxliii. 7), the silver salt of this acid is formed on digesting a solution of *a*-chloropropionic acid with an excess of argentic hydroxide. It crystallizes in bundles of glistening needles. The free acid is a syrup; it is converted into glyceric acid by nascent hydrogen.

(1821) **Dehydro-*a*-*β*-dihydroxybutyric Acid**: $C_4H_6O_3 = C_3H_5O.COOH$.—This acid is obtained by converting the chloropropylenic oxide (so-called epichlorhydrin) $O\left\{\begin{array}{l}CH_2\\ \;|\\ CH.CH_2Cl\end{array}\right.$ into the corresponding cyano-derivative by careful treatment with a dilute aqueous solution of *pure* potassic cyanide, and boiling this compound with hydrochloric acid. It crystallizes in glistening prisms melting at 225° (437° F.), easily soluble in hot, but difficultly in cold water (Pazschke, *Jour. pr. Chem.* [2], i. 97; Hartenstein, *ibid.*, vii. 295).

It does not unite with hydrochloric acid; heated with hydriodic acid, it yields butyric acid.

(1822) **Acetoacetic Acid**: $CH_3.CO.CH_2.COOH$.—This acid cannot exist either in the free state or in the form of a metallic salt, but its ethereal salts are stable compounds and are of great importance as synthetical agents. These salts are prepared from the corresponding acetates by the action of sodium; the nature of the reaction involved in their formation has been the subject of much discussion.

Löwig and Weidmann, in 1840 (*Pogg. Ann.* l. 95), in the course of an investigation on the action of the alkali metals on various ethereal salts, observed that ethylic acetate was violently attacked by potassium without any gas being evolved, but they did not definitely establish the nature of the reaction, and the subject did not again attract the attention of chemists until 1863—1865. In the former year, Geuther stated (*Göttinger Anzeigen*, 1863, p. 281) that ethylic acetate was capable of dissolving about 12 per cent. of its weight of sodium with evolution of hydrogen, and that the final product was a mixture of sodic ethylate and a sodium compound of the formula $C_6H_9NaO_3$, produced in accordance with the equation: $2C_4H_8O_2 + 2Na = H_2 + C_2H_5ONa + C_6H_9NaO_3$; the latter compound was isolated in a pure state, and its properties most carefully ascertained, and it was shown that by heating it in a current of hydrochloric acid gas the corresponding hydrogen compound $C_6H_{10}O_3$ could be obtained, and that by treating it with methylic and ethylic iodide, the sodium could be displaced by methyl and ethyl. Holding peculiar views as to the constitution of acetic acid, Geuther assigned peculiar rational formulæ and names to these compounds, terming, for example, the compound $C_6H_{10}O_3$, "*dimethylencarbonsäureäthylenäther*" or *diacetsäureäther*, and representing it by the formula (old notation)

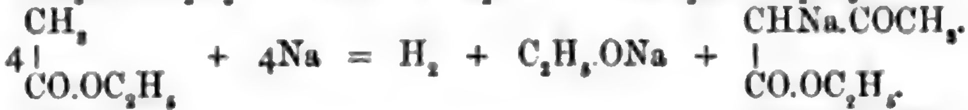
$$\left.\begin{array}{l}C_2H_2, C_2O_2\\ C_2H_2, C_2O_2\end{array}\right\}\begin{array}{l}HO\\ HO, C_4H_4,\end{array} \text{ acetic acid being } C_2H_2, C_2O_2\left\{\begin{array}{l}HO\\ HO\end{array}\right.;$$

but he subsequently (*Jenaische Zeitschrift f. Medecin u. Naturw*, 1865, 387) somewhat modified his views, and termed the compound $C_6H_{10}O_3$ ethyldiacetic *acid* instead of diacetic *ether*, as he found that it was capable of exchanging an atom of hydrogen for metals.

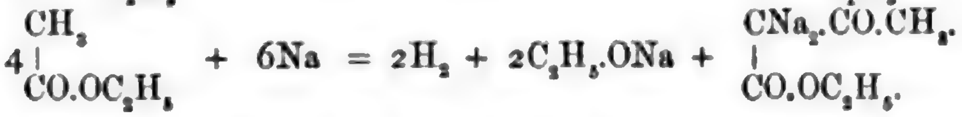
Meanwhile Frankland and Duppa published a most important memoir (*Phil. Trans.*, clvi. 37), in which they described the product obtained on dissolving as much sodium as possible in ethylic acetate and at once treating the entire crude product with moniodo-paraffins. Using ethylic iodide they obtained four distinct products, viz., *ethylic ethacetate*, $C_2H_5.CH_2.COOC_2H_5$, *ethylic diethacetate*, $(C_2H_5)_2CH.COOC_2H_5$, *ethylic ethacetonecarbonate*, $CH_3.CO.CH(C_2H_5).COOC_2H_5$—a substance having all the properties described by Geuther as characteristic of that produced on treating the compound $C_6H_9NaO_3$ with ethylic iodide, and *ethylic diethacetonecarbonate* $CH_3.CO.C(C_2H_5)_2.COOC_2H_5$. Analogous compounds were obtained when other moniodo-paraffins were employed. In order to explain the formation of these different bodies, Frankland and Duppa assumed that three other sodium compounds were formed besides that isolated by Geuther, and represented the action of sodium on ethylic acetate by the following equations:

I. $2CH_3.COOC_2H_5 + 2Na = H_2 + 2CH_2Na.COOC_2H_5.$

II. $CH_3.COOC_2H_5 + 2Na = H_2 + CHNa_2.COOC_2H_5.$

III.


$$4\begin{array}{l}CH_3\\ | \\ CO.OC_2H_5\end{array} + 4Na = H_2 + C_2H_5.ONa + \begin{array}{l}CHNa.COCH_3.\\ | \\ CO.OC_2H_5.\end{array}$$

IV.


$$4\begin{array}{l}CH_3\\ | \\ CO.OC_2H_5\end{array} + 6Na = 2H_2 + 2C_2H_5.ONa + \begin{array}{l}CNa_2.CO.CH_3.\\ | \\ CO.OC_2H_5.\end{array}$$

From these various compounds, the above-named ethylic derivatives were supposed to be formed by the direct displacement of the sodium by ethyl.

Geuther maintained, however, that no other sodium derivatives than the two he had isolated were formed in the reaction, and stated as a further proof of the correctness of the equation $2C_4H_8O_2 + 2Na = H_2 + C_2H_5ONa + C_6H_9NaO_3$ that almost the theoretical amount of "ethyldiacetic acid" could be obtained by dissolving sodium in a large excess of ethylic acetate, distilling off as far as possible the excess of the latter on the water bath, dissolving the residue in water, adding an amount of acetic acid equivalent to the sodium employed, and extracting with ether (*Zeits. Chem.*, 1866, 439; 1868, 58). He suggested that the ethacetate, diethacetate and diethacetonecarbonate obtained by Frankland and Duppa were probably formed from the ethacetonecarbonate resulting from the action of ethylic iodide on the sodium compound $C_6H_9NaO_3$ by the action of the sodic ethylate or by the combined action of sodic ethylate and ethylic acetate, and actually succeeded in obtaining ethylic ethacetate by heating a mixture of ethylic ethacetonecarbonate, ethylic acetate and sodic ethylate at 120° (248° F.) (*ibid.*, 1869, 27), but he did not show that the two other compounds could be produced in this manner.

Geuther's experiments for a long time were not estimated at their proper value, and chemists continued to believe in the possibility of forming the sodium derivatives corresponding with the ethylated compounds obtained by Frankland and Duppa; any doubt as to the correctness of his interpretation of the action of sodium on ethylic acetate has been rendered impossible, however, by the recent important researches of Wislicenus (comp. *Ann. Chem. Pharm.*, clxxxvi. 61). This chemist finds that ethylic acetoacetate (Geuther's ethyldiacetic acid), $CH_3.CO.CH_2.COOC_2H_5$, is capable of exchanging only one atom of hydrogen for sodium when submitted to the action of this metal, forming Geuther's compound $C_6H_9NaO_3 = CH_3.CO.CHNa.COOC_2H_5$, but that if the sodium in this body be displaced by ethyl, a substance is produced which is also capable of exchanging an atom of hydrogen for sodium, forming ethylic acetosodethacetate, $CH_3.CO.CNa(C_2H_5).COOC_2H_5$; by treating this latter compound with ethylic iodide, ethylic acetodiethacetate, $CH_3.CO.C(C_2H_5)_2.COOC_2H_5$, is produced, and upon this body sodium has no action whatever. He also finds that sodic ethylate may be employed instead of sodium in preparing these sodium compounds, and that if the sodium compounds, or the mixture of sodic ethylate and acetoacetate, acetoethacetate or acetodiethacetate be heated, a complex mixture of decomposition products is obtained, chief among which is the ethylic salt of the acid of the acetic series from which the acetoacetate is derived. Ethylic acetosodacetate, for example, yielding ethylic acetate, and ethylic ethacetate or butyrate being formed from the sodethacetate. These facts enable us to explain Frankland and Duppa's results. In the first instance, by the action of the sodium on the ethylic acetate, a mixture of ethylic acetosodacetate and sodic ethylate is produced; on treating this with ethylic iodide, the former is partially converted into ethylic acetoethacetate, and the latter partially converted into ethylic ether; the acetoethacetate thus formed, however, partly enters into reaction with the unattacked sodic ethylate, and the resulting acetosodethacetate is in turn transformed into acetodiethacetate; but being in presence of sodic ethylate, the acetoethacetate and acetodiethacetate thus produced partially undergo decomposition into ethylic ethacetate and diethacetate respectively. A precisely similar explanation may be given of the formation of the corresponding methyl and isopropyl derivatives which are produced when methylic and isopropylic iodides are employed.

Löwig and Weidmann observed that potassium dissolved in ethylic acetate without evolution of gas, but according to Geuther and Frankland and Duppa hydrogen is always evolved in considerable quantity on dissolving sodium in ethylic acetate; Wanklyn, however, has maintained that no hydrogen is produced when pure ethylic acetate is heated with sodium (*Ann. Chem. Pharm.*, cxlix. 43), and that the action takes place in accordance with the equation:

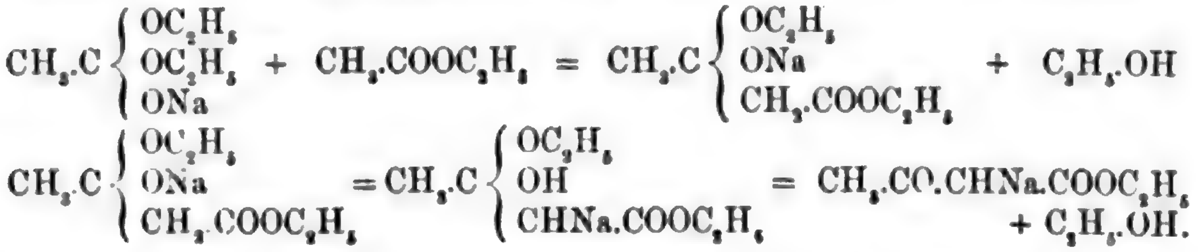
$$\underset{\text{Ethylic acetate.}}{3CH_3.COOC_2H_5} + 4Na = \underset{\text{Sodic ethylate.}}{3C_2H_5ONa} + \underset{\text{Sodium triacetyl.}}{Na(CO.CH_3)_3},$$

but without advancing the slightest experimental evidence of the truth of this equation; Ladenburg also has stated (*Deut. chem. Ges. Ber.*, iii. 305) that ethylic acetate purified from alcohol by treatment with silicic chloride or phosphoric oxychloride is only slowly attacked by sodium at 100° (212° F.) and that no hydrogen is produced; and according to Oppenheim and Precht (*ibid.*, ix. 318) the acetate when distilled from phosphoric anhydride dissolves sodium without evolution of hydrogen. The amount of hydrogen obtained by Frankland and Duppa was too large, however, to have been produced entirely from alcohol present as impurity in the acetate employed (comp. *Proc. Roy. Soc.*, 1870, 228), and Geuther's experiments leave little doubt as to the correctness of the equation: $2CH_3.COOC_2H_5 + 2Na = H_2 + C_2H_5ONa + CH_3.CO.CHNa.COOC_2H_5$ as an expression of the primary reaction. Probably the hydrogen enters into secondary reactions; but apparently the extent to which this takes place varies according as the acetate is free from, or contains, alcohol.

Geuther has shown that ethylic acetosodacetate may be obtained by heating ethylic acetate with sodic ethylate free from alcohol at 130° (266° F.), and that it is also formed, although in less quantity, when the crystallized ethylate (p. 429) is employed (*Zeits. Chem.*, 1868, 652); according to Oppenheim and Precht (*loc. cit.*), a certain amount is produced on merely heating a mixture of an alcoholic solution of sodic ethylate with ethylic acetate for several hours at its boiling point. If such a mixture as this last be submitted to distillation from the water-bath, the ethylic acetate passes over unchanged (Geuther); but according to Wanklyn (*Ann. Chem. Pharm.*, cl. 205), pure sodic ethylate, $NaOC_2H_5$, combines with ethylic acetate, and on heating the mixture at 100°—200° (212°—392° F.) alcohol distils over. These observations are of considerable importance in connexion with the question as to the manner in which ethylic acetosodacetate is produced, and together with the fact that the action of sodium on *pure* ethylic acetate takes place with extreme slowness, whereas the ordinary acetate, which undoubtedly contains alcohol, is very readily attacked, they lend considerable support to the view that sodic ethylate and not sodium is the real agent in effecting the conversion. It appears not improbable that a compound of the ethylate with the acetate is first produced, thus:

$$CH_3.CO.OC_2H_5 + C_2H_5ONa = CH_3.C(OC_2H_5)_2.(ONa),$$

and that this enters into reaction with a second molecule of acetate, ultimately forming ethylic acetosodacetate and alcohol, perhaps as shown by the equations:



$$CH_3.C\left\{\begin{matrix}OC_2H_5\\OC_2H_5\\ONa\end{matrix}\right. + CH_3.COOC_2H_5 = CH_3.C\left\{\begin{matrix}OC_2H_5\\ONa\\CH_3.COOC_2H_5\end{matrix}\right. + C_2H_5.OH$$

$$CH_3.C\left\{\begin{matrix}OC_2H_5\\ONa\\CH_2.COOC_2H_5\end{matrix}\right. = CH_3.C\left\{\begin{matrix}OC_2H_5\\OH\\CHNa.COOC_2H_5\end{matrix}\right. = CH_3.CO.CHNa.COOC_2H_5 + C_2H_5.OH.$$

(1823) *Preparation of ethylic acetoacetate.*—Conrad and Wislicenus (*Ann. Chem. Pharm.*, clxxxvi. 214) give the following instructions for preparing this compound by Geuther's method:—1000 grams of ethylic acetate are placed in a flask provided with an efficient reversed condenser and 100 grams of sodium in pieces of about the cubic contents of a pea are added at once. The liquid soon enters into ebullition, much heat being developed; when the reaction slackens, heat is applied by means of a water-bath until the sodium is completely dissolved, which is usually effected in from 2 to 2½ hours. The still warm mass is then mixed with 550 grams of 50 per cent. acetic acid, the mixture is allowed to cool, about ½ a litre of water is added and the whole well agitated. The upper layer is now separated, washed with a little water, and heated in a copper vessel on the water-bath to drive off as much as possible of the unchanged ethylic acetate; the residue is then fractionally distilled from a glass vessel, collecting apart the portions which come over at 100°—130°, 130°—165°, 165°—175°, 175°—185°, and 185°—200° C. After refractionating these distillates, collecting between the same limits of temperature, the distillates at 100°—175° and 185°—200° C. are reduced to very small amounts, and the fraction boiling at 175°—185° C. is sufficiently pure for most purposes, but may be further purified by fractionation; too frequent distillation is to be avoided, however, as a small amount of the acetoacetate is decomposed at each distillation into lower boiling products and dehydracetic acid (1832). The maximum amount produced in this manner is 175 grams, but considerably less is obtained if a longer time be taken in dissolving the sodium, or, what amounts to the same thing, if a larger quantity of acetate be employed. A considerable amount of ethylic acetate may be recovered by washing the distillate collected below 100° C. with a saturated solution of sodic chloride to remove alcohol, drying over calcic chloride and rectifying.

(1824) *Properties.*—Ethylic acetoacetate is a mobile colourless liquid of fruity odour, somewhat soluble in water, of the sp. gr. 1·03 at 5° (41° F.); it boils at 181° (357°·8 F.). Its aqueous solution is coloured dark violet by ferric chloride. It passes over unchanged with vapour of water, but if heated with water at 150° (302° F.), it is decomposed into dimethylketone or acetone, ethylic alcohol and carbonic acid: $CH_3.CO.CH_2.COOC_2H_5 + 2OH_2 = CH_3.CO.CH_3 + CO(OH)_2 + C_2H_5.OH$; in presence of mineral acids or alkalies this decomposition takes place much more readily (comp. 1819). It is converted into β-hydroxybutyric acid by the action of nascent hydrogen (1807). On oxidation, by a very dilute solution of potassic permanganate, it yields acetic and oxalic acid. It combines with hydrocyanic acid, forming a cyanide which is convertible into hydroxypyrotartaric acid. It also combines with a single molecule of bromine, forming an unstable dibromide, $C_6H_{10}O_3Br_2$ (Lippmann), but if treated with an excess of bromine it appears to form a dibromodibromide, $C_6H_8O_3Br_4$; chlorine is readily absorbed by it, a considerable amount of heat being developed and pure hydrochloric acid evolved: the product is a colourless liquid, boiling at 206° (402°·8 F.); it is with difficulty decomposed by water, but if heated with dilute hydrochloric acid at 170°—180° (338°—356° F.), it is resolved into dichloracetone, $CH_3.CO.CHCl_2$, carbonic acid and ethylic alcohol; if decomposed with an aqueous or alcoholic solution of potassic hydrate, however, it furnishes a mixture of acetate and dichloracetate, and is thus shown to be ethylic acetodichloracetate, so that the action of chlorine is represented by the equation (Conrad, *ibid.*, clxxxvi. 232):

$$CH_3.CO\,CH_2.COOC_2H_5 + 2Cl_2 = CH_3\,CO.CCl_2.COOC_2H_5 + 2HCl.$$

The monochlorinated compound has been obtained by heating ethylic acetoacetate with suphuric dichloride, SO_2Cl_2 (Allihn, *Deut. chem. Ges. Ber.*, xi. 567). Ethylic acetoacetate is readily attacked by phosphoric pentachloride, a mixture of hydrochloric acid and ethylic chloride being evolved; probably the first action consists in the formation of ethylic dichlorobutyrate: $PCl_5 + CH_3.CO.CH_2.COOC_2H_5 = CH_3.CCl_2.CH_2.COOC_2H_5$, but this decomposes into hydrochloric acid and a mixture of the ethylic salts of two isomeric chlorocrotonic acids: $C_3H_5Cl_2.COOC_2H_5 = C_3H_4Cl.COOC_2H_5 + HCl$; the hydrochloric acid, however, partially decomposes these ethylic salts, forming ethylic chloride and the corresponding acids, and these latter are converted into the acid chloride by the action of the pentachloride, so that finally a mixture of the acid chlorides and of the ethylic salts of the two chlorocrotonic acids is obtained. A considerable amount of a resinous substance is also produced (Geuther, *Jour. pr. Chem.* [2], iii. 432). If well cooled ethylic acetoacetate be saturated with ammonia, a crystalline highly deliquescent substance of the formula $C_6H_{11}NO_2 = C_6H_{10}O_3 + NH_3 - OH_2$ is produced (Precht, *ibid.*, xi. 1193); aniline also readily decomposes it with formation of acetone, alcohol and diphenylcarbamide, $CO(NH.C_6H_5)_2$ (*ibid.*, ix. 1098).

If the mixture of sodic ethylate and ethylic acetosodacetate produced by treating ethylic acetate with sodium be gently warmed with carbonic bisulphide, a violent reaction takes place; the product, when purified by crystallization from water, forms brick-red coloured needles of the composition $C_{10}H_{12}S_2NaO_4$. The formation of this body may be explained by supposing that the bisulphide combines with the acetosodacetate, and that the resulting compound then enters into reaction with the sodic xanthate formed by the union of another portion of the bisulphide with sodic ethylate; thus:

$$CH_3.CO.CHNa.COOC_2H_5 + CS_2 = CH_3.CO.CH(CSSNa).COOC_2H_5.$$

$$CH_3.CO.CH(CSSNa).COOC_2H_5 + C_2H_5O.CSSNa = CH_3.CO.C(CSSNa)\left\{\begin{matrix} COOC_2H_5 \\ CSOC_2H_5 \end{matrix}\right. + NaSH.$$

If a mixture of ethylic acetoacetate and carbonic bisulphide be heated with plumbic or zincic oxide in sealed tubes at 100° (212° F.), a compound of the formula $C_7H_8SO_3$, crystallizing in straw-yellow needles, is produced; it may be represented as formed in the following manner (Norton and Oppenheim, *ibid.*, x. 701): $CH_3.CO.CH_2.COOC_2H_5 + CS_2 + PbO = CH_3.CO.C(CS).COOC_2H_5 + PbS + OH_2$. Ethylic acetosodacetate enters directly into reaction with diazo-salts in the manner represented by the equation $R'.N_2.NO_3 + CH_3.CO.CHNa.COOC_2H_5 = CH_3.CO.CH(N_2.R').COOC_2H + NaNO_3$; the resulting compounds crystallize well, and are decomposed with remarkable facility by alkalies, forming metallic salts of the corresponding acetoacetic acid derivatives, from which the free acids may be obtained (V. Meyer, *ibid.*, x. 2075; Züblin, xi. 1417).

(1825) *Metallic derivatives of ethylic acetoacetate.*—Ethylic acetoacetate is capable of exchanging one of its atoms of hydrogen not only for sodium but for metals generally, forming a series of well-characterized metallic derivatives of the formula $CH_3.CO.CHM'.COOC_2H_5$. *Ethylic acetosodacetate* is best prepared in the solid state by dissolving sodium in about ten times its weight of anhydrous alcohol, adding to the cold crystalline mass an equal volume of ether, and treating the mixture with the equivalent quantity of ethylic acetoacetate also diluted with an equal volume of ether; on adding about 2 c.c. of water and stirring well, it separates as a crystalline precipitate, which may be pressed and dried over sulphuric acid (Harrow, *Jour. Chem. Soc. Trans.*, 1878, 427). It crystallizes from a mixture of ether with a small quantity of alcohol in feathery needles (Geuther). Probably this compound is also formed on dissolving ethylic acetoacetate in a dilute solution of sodic hydrate, and the corresponding potassium and barium derivatives may be produced in a similar manner. By adding cupric acetate to a solution of the barium derivative (Geuther), or by shaking the acetoacetate with an ammoniacal solution of cupric sulphate (Conrad), *ethylic acetocupracetate*, $C_{12}H_{18}O_6Cu$, is obtained as a pale-green precipitate insoluble in water; it crystallizes from hot benzene, alcohol, or ethylic iodide in glistening needles, melting at 182° (359°·6 F.). The corresponding cobalt and nickel derivatives are produced by shaking ethylic acetoacetate with solutions of cobalt and nickel sulphate containing ammonia and ammonic chloride; they crystallize from hot benzene in microscopic plates. The magnesium compound may be prepared in a precisely similar manner, or by the action of magnesium amalgam on ethylic acetoacetate, and crystallizes from benzene in glistening plates, which melt at 240° (464° F.) with decomposition. If ethylic acetoacetate be added to a solution of potassic aluminate, the liquid, which is at first clear, after a few hours becomes filled with glistening crystals of the aluminium derivative $(C_6H_9O_3)_6Al_2$; this compound is very soluble in ether, benzene and carbonic bisulphide; it melts at 76° (168°·8 F.), and may be distilled unchanged (Conrad, *Ann. Chem. Pharm.*, clxxxviii. 269).

(1826) *Action of sodium on ethereal acetates other than ethylic acetate.*—Brandes (*Zeits. Chem.*, 1866, 454), Oppenheim and Precht (*Deut. chem. Ges. Ber.*, ix. 1097), and Conrad (*Ann. Chem. Pharm.*, clxxxvi. 228), respectively have shown that methylic, isobutylic and isamylic acetates behave as ethylic acetate on treatment with sodium; hence it would appear that the acetates of the formula $CH_3.COOC_nH_{2n+1}$ may all be converted into the corresponding acetoacetates, $CH_3.CO.CH_2.COOC_nH_{2n+1}$, by the action of sodium.

Conrad and Hodgkinson (*Ann. Chem. Pharm.*, cxciii. 298) find, however, that benzylic acetate, propionate, and butyrate furnish as chief products a mixture of the sodic salt of the corresponding acid of the acetic series with the benzylic salt of a benzyl derivative of the same acid; and Hodgkinson has obtained similar results with benzylic isobutyrate (*Chem. Soc. Jour. Trans.*, 1878, p. 495). The action of sodium on benzylic salts of primary and secondary acids of the acetic series may therefore be expressed by the equation:

$$4\begin{array}{l}C_nH_{2n+1}\\|\\COOCH_2.C_6H_5\end{array} + 2Na = 2\begin{array}{l}C_nH_{2n+1}\\|\\COONa\end{array} + 2\begin{array}{l}C_nH_{2n}.CH_2.C_6H_5\\|\\COOCH_2.C_6H_5\end{array} + H_2.$$

But other products are simultaneously formed: for example, benzylic acetate also yields toluene and the sodic salts of cinnamic and hydrocinnamic acids, together with a certain amount of benzylic dibenzylacetate; the benzylic salts of the homologous primary acids furnish corresponding bodies, but benzylic isobutyrate behaves in a different manner. These results show that the reaction is of a complex character; and although, at present, the necessary data for its correct interpretation do not appear to exist, it is of interest in connexion with this question that ethylic acetobenzylacetate does not furnish a normal product on treatment with alkali, but is converted into dibenzylacetate (*Ann. Chem. Pharm.*, clxxxvii. 11).

(1827) *Production of compounds of the form* $CH_3.CO.CHX.COOC_2H_5$ *and* $CH_3.CO.CXY.COOC_2H_5$ *from ethylic acetoacetate.*—It has already been pointed out that a series of homologues of ethylic acetoacetate of the form $CH_3.CO.CH(C_nH_{2n+1}).COOC_2H_5$ may be prepared by acting on the acetoacetate with sodium and treating the resulting acetosodacetate with bodies such as ethylic iodide; and that by repeating these operations a series of homologues of the form $CH_3.CO.C(C_nH_{2n+1})_2.COOC_2H_5$ may be obtained. The radicle introduced at the second operation may either be the same or different from that introduced at the first; and besides the haloid compounds of the C_nH_{2n+1} radicles very many other haloid compounds of the form R′ (Cl, Br, I), such as ethylic monochloracetate, &c., may be employed.*

Wislicenus has described at length the precautions which should be adopted in preparing such derivatives (*Ann. Chem. Pharm.*, clxxxvi. 216). He recommends that the ethylic acetoacetate be mixed with about an equal volume of pure benzene, and that the solution be digested with an excess of sodium in a flask attached to a reversed condenser; the excess of sodium having been removed by means of a glass spoon, an amount of the haloid compound equivalent to the amount of sodium dissolved is then run in, and the mixture digested, if necessary, on the water-bath. Afterwards sufficient water is added to dissolve the sodic chloride, bromide or iodide, and the aqueous solution separated from the solution of the product in benzene; the latter is washed by agitation with a small quantity of water, dried by means of potassic carbonate or some other suitable desiccating agent, the benzene distilled off on the water-bath, and the

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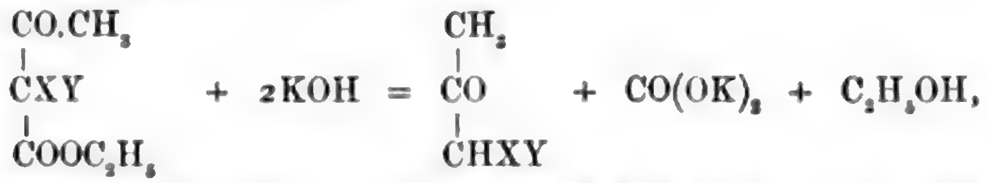
* The following is a list of the compounds hitherto prepared:

1.	Ethylic	acetomethacetate	$Ac.CH(CH_3).COOEt$
2.	,,	acetodimethacetate	$Ac.C(CH_3)_2.COOEt$
3.	,,	acetoethacetate	$Ac.CH(C_2H_5).COOEt$
4.	,,	acetomethethacetate	$Ac.C(CH_3)(C_2H_5).COOEt$
5.	,,	acetodiethacetate	$Ac.C(C_2H_5)_2.COOEt$
6.	,,	acetoisopropacetate	$Ac.CH(C_3H_7^{\beta}).COOEt$
7.	,,	acetoisobutylacetate	$Ac.CH(C_4H_9^{\beta}).COOEt$
8.	,,	acetodiisobutylacetate	$Ac.C(C_4H_9^{\beta})_2.COOEt$
9.	,,	acetoallylacetate	$Ac.CH(C_3H_5).COOEt$
10.	,,	acetodiallylacetate	$Ac.C(C_3H_5)_2.COOEt$
11.	,,	acetobenzylacetate	$Ac.CH(CH_2.C_6H_5).COOEt$
12.	,,	acetobenzylmethacetate	$Ac.C(CH_3)(C_7H_7).COOEt$
13.	,,	acetobenzylethacetate	$Ac.C(C_2H_5)(C_7H_7).COOEt$
14.	,,	acetobenzoylacetate	$Ac.CH(CO.C_6H_5).COOEt$
15.	,,	acetomalonate	$Ac.CH(COOEt)_2$
16.	,,	acetosuccinate	$Ac.CH.COOEt$ | $CH_2.COOEt$
17.	,,	aceto-α-propanedicarboxylate	$Ac.CH.COOEt$ | $CH_2.CH_2.COOEt.$

residue purified by rectification; or, if it cannot be distilled unchanged, exposed over sulphuric acid *in vacuo* until it ceases to lose weight. A similar course is adopted in converting the mono-derivatives thus obtained into di-derivatives. In operating in this manner, however, there is always a certain amount of resinous bye-product formed owing to the partial decomposition of the sodium derivative which takes place during the prolonged heating necessary to effect the solution of the necessary amount of sodium, and probably also to the action of the nascent hydrogen. According to Conrad and Limpach (*ibid.*, cxcii. 153), this is not the case if sodic ethylate be employed in place of sodium. They direct that an amount of sodium equivalent to the amount of acetoacetate to be employed be dissolved in 10—12 times its weight of anhydrous alcohol, and that when cool this solution be mixed with the acetoacetate, the haloid compound being then immediately added; the reaction is either moderated by cooling, or allowed to proceed unchecked, or assisted by warming, according to circumstances, and is considered to be complete when the liquid is no longer alkaline. The greater part of the alcohol is then distilled off on the water-bath, the residue is mixed with water, and the upper oily layer submitted to distillation.

(1828) *Action of alkalies on ethylic acetoacetate and its derivatives.*—Ethylic acetoacetate was shown by its discoverer to be decomposed by alkalies into acetone, alcohol and carbonic acid, and Frankland and Duppa observed that the substituted derivatives which they obtained were decomposed in a manner precisely analogous; the researches of Wislicenus and his pupils have shown, however, that in addition to this mode of decomposition, which may be represented by the following general equation:

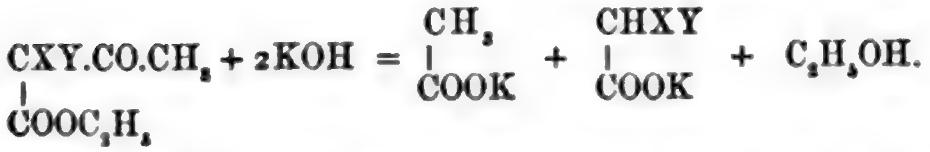


$$\begin{matrix} CO.CH_3 \\ | \\ CXY \\ | \\ COOC_2H_5 \end{matrix} + 2KOH = \begin{matrix} CH_3 \\ | \\ CO \\ | \\ CHXY \end{matrix} + CO(OK)_2 + C_2H_5OH,$$

ethylic acetoacetate and the compounds derived from it also undergo the following change:

18.	Ethylic	acetomethylsuccinate	$Ac.CH.COOEt$ $\vert$ $CH(CH_3).COOEt$
19.	„	„	$Ac.C(CH_3).COOEt$ $\vert$ $CH_2.COOEt$
20.	„	acetomethylpyrotartrate	$Ac.C(CH_3).COOEt$ $\vert$ $CH_2.CH_2.COOEt$
21.	„	acetodimethylsuccinate	$Ac.C(CH_3).COOEt$ $\vert$ $CH(CH_3).COOEt$
22.	„	acetoethylsuccinate	$Ac.C(C_2H_5).COOEt$ $\vert$ $CH_2.COOEt$
23.	„	„	$Ac.CH.COOEt$ $\vert$ $CH(C_2H_5).COOEt$
24.	„	acetotricarballylate	$Ac.C(CH_2.COOEt)_2$ $\vert$ $COOEt.$

In these formulæ $Ac = CH_3.CO$; $Et = C_2H_5$. Compare Frankland and Duppa and Geuther, *loc. cit.*; *Ann. Chem. Pharm.* clxxxvi., clxxxvii., clxxxviii., cxc., cxcii., cxciii.; *Deut. chem. Ges. Ber.*, x. 1956; xi. 1055.



$$\underset{\displaystyle |\atop \displaystyle COOC_2H_5}{CXY}.CO.CH_3 + 2KOH = \underset{COOK}{\overset{CH_3}{|}} + \underset{COOK}{\overset{CHXY}{|}} + C_2H_5OH.$$

The extent to which these two kinds of change take place depends not only on the nature of the compound, but also on the conditions observed in effecting the decomposition. If an aqueous solution of baric hydrate be employed as hydrating agent, the corresponding acetone or compound of the form $CH_3.CO.CHXY$ is almost exclusively produced; but if an alcoholic solution of potassic hydrate be used, a considerable amount undergoes conversion in accordance with the second equation, and the extent to which the decomposition into a molecule of acetate and a molecule of the salt $CHXY.COOK$ takes place is greater the more concentrated the alkaline solution both initially and at the close of the operation. This is clearly shown by the following results obtained with ethylic ethacetate (Wislicenus, *Ann. Chem. Pharm.*, cxc. 257):

Concentration of KOH solution.		No. of mols. KOH employed to 1 mol. ethylic salt.	Percentage of ethylic salt converted		
at beginning of change.	at end of change.		into ketone, &c.	into acetate and ethacetate.	Total.
Baric hydrate.			98·38	1·42	99·80
1·40	·25	2·24	88·54	3·83	92·37
11·20	6·40	4·70	91·05	8·74	99·79
11·76	3·79	3·02	98·42	3·98	102·40
15·66	6·70	3·34	88·38	10·83	99·21
16·80	2·92	2·36	82·61	14·73	97·34
16·80	9·57	4.68	76·28	24·25	100·53
22·40	12·69	4.62	58·80	41·40	100·20
24·64	2·78	2·26	80·41	19·81	100·21
24·86	3·70	2·25	81·82	14·14	95·69

The difference in the behaviour of different acetoacetates under similar conditions will be evident on inspection of the following Table, which exhibits the results obtained by decomposing the ethylic salts by two different solutions of potassic hydrate employed in the proportion of 2·75 mols. KOH to 1 mol. of the salt:

	Percentage converted by a 10·27—10·4 per cent. solution into		Percentage converted by a 20·54—20·8 per cent. solution into	
	ketone, &c.	acids.	ketone, &c.	acids.
Ethylic acetoacetate . . .	81·87	17·43	60·03	41·03
„ acetomethacetate .	86·28	13·70	68·16	31·20
„ acetoethacetate . .	91·52	8.75	75·44	23·75
„ acetodimethacetate	91·73	7·46	80·02	19·96
„ acetoallylacetate .	82·42	17·54	51·14	?
„ acetodiethacetate .	54·15	42·50	30·86	6·94

It will be observed that whereas ethylic acetoethacetate yields relatively more ketone and a smaller amount of acids than the acetodiethacetate, ethylic acetodimethacetate yields more ketone and a smaller amount of acids than the acetomethacetate; but the two compounds ethylic acetoethacetate and dimethacetate, which have the same molecular weight, furnish very similar values.

(1829) Action of Nitrous Acid on Ethylic Acetoacetate and Homologous Compounds.—If ethylic acetoacetate (1 mol. proportion) be dissolved in a dilute solution of potassic hydrate (1 mol. proportion), and a solution of potassic nitrite (1 mol. proportion) be then added, and the liquid rendered acid with dilute sulphuric acid, the nitrous acid thus set at liberty reacts upon the acetoacetate, forming *ethylic acetonitrosoacetate*, $CH_3.CO.CH(NO).COOC_2H_5$. The unattacked acetoacetate may be recovered by rendering the solution alkaline and extracting with ether; if the solution be then acidified and again extracted with ether, the acetonitrosoacetate is dissolved: on carefully distilling off the ether, and exposing the residue over sulphuric acid *in vacuo*, it remains as an oil which crystallizes with difficulty unless a previously obtained crystal be added. If, after extracting the unattacked acetoacetate, the alkaline solution be allowed to stand several days, the acetonitrosoacetate undergoes decomposition, forming *nitrosodimethylketone* or *nitrosoacetone*, $CH_3.CO.CH_2(NO)$.

Ethylic acetomethacetate appears to behave similarly, but the resulting nitroso-derivative at once undergoes further decomposition, yielding (1) *methylnitrosoethylketone*, $CH_3.CO.CH(NO).CH_3$, when an excess of aqueous potassic hydrate is employed; (2) *ethylic β-nitrosopropionate*, $CH_3.CH(NO).COOC_2H_5$, when an alcoholic solution of a single mol. proportion of potassic hydrate is used; and (3) *β-nitrosopropionic acid*, $CH_3.CH(NO).COOH$, when the alkaline solution of ethylic β-nitrosopropionate is allowed to stand. Ethylacetoethacetate furnishes only *methylnitrosopropylketone*, $CH_3.CO.CH(NO).CH_2.CH_3$.

These nitroso-compounds are all crystalline, and exhibit acid properties; nitrosodimethylketone melts at 65° (149° F.), and does not volatilize unchanged unless a very minute amount be heated; methylnitrosoethylketone melts at 74° (165°·2 F.), and boils without the slightest decomposition at 185° (365° F.); methylnitrosopropylketone melts at 54° (129°·2 F.), and partially decomposes on distillation (V. Meyer; V. Meyer and Züblin, *Deut. chem. Ges. Ber.*, x. 2076; xi. 320, 692).

(1830) Action of Sodium on Ethylic Salts of Homologues of Acetic Acid. *Action on ethylic formate.*—Löwig and Weidmann, who first studied the action of sodium on this compound, observed the formation of ethylic alcohol, sodic formate, carbonic oxide and a small quantity of brown resinous product; Greiner, who subsequently examined the reaction (*Zeits. Chem.*, 1866, 460), obtained hydrogen and sodic ethylate also. Wanklyn maintains, however (*Chemical News*, 1868, xviii., 143), that pure carbonic oxide is evolved, and he further states that a mixture of ethylic formate and alcohol does not furnish hydrogen when acted on by sodium.

Geuther has shown (*Zeits. Chem.*, 1868, 655) that ethylic formate is completely resolved into carbonic oxide and alcohol by merely warming with sodic ethylate, the decomposition commencing even at ordinary temperatures; it is therefore probable that when ethylic formate of ordinary purity is treated with sodium, its decomposition is in the main, if not entirely, the result of the action of sodic ethylate formed, in the first instance, from traces of alcohol present, and subsequently from that produced in the reaction which may be supposed to take place in the manner indicated by the following equations:

$$H.COOC_2H_5 + C_2H_5ONa = H.C(OC_2H_5)_2(ONa);$$
$$H.C(OC_2H_5)_2(ONa) = CO + C_2H_5.ONa + C_2H_5.OH.$$

Action of Sodium on Ethylic Propionate.—By treating this compound with sodium and decomposing the resulting sodium compound with acetic acid, &c., as in the preparation of ethylic acetoacetate, Hellon and Oppenheim (*Deut. chem. Ges. Ber.*, x. 699) have obtained *ethylic propiopropionate*, $C_8H_{14}O_3$, as a colourless, pleasant-smelling liquid, boiling at about 200° (392° F.). Like ethylic acetoacetate, this compound dissolves sodium with evolution of hydrogen, but it is not coloured by ferric chloride, nor does it react with mercuric oxide. From the manner in which it is formed, it probably has the constitution represented by the formula $CH_3.CH(CH_3.CH_2.CO).COOC_2H_5$.

Action of Sodium on Ethylic Isovalerate.—The reaction in this case appears to be of a highly complex character. According to Greiner (*Zeits. Chem.*, 1866, 461), scarcely any hydrogen is evolved, and on adding water to the product an oily liquid separates, which may be resolved by fractional distillation into portions boiling below 100°, at 130°—140°, at 180°—190°, at 200°—210°, at about 230°, and at 250°—300° C. The chief product is that boiling at the highest temperature, and to this the formula $C_{10}H_{18}O$ is assigned; next in importance is that boiling at 200°—210°, which has the formula $C_{12}H_{24}O_2$. The portion boiling at 230° when kept crystallizes in long needles, melting at 65°, and perhaps has the composition $C_{22}H_{48}O_5$. The portion of lowest-boiling point is a mixture of alcohol with a small amount of ethylic isovalerate, that boiling at 130°—140° being the almost pure isovalerate; the results obtained on analyzing the portion boiling at 180°—190° are expressed by the formula $(C_{20}H_{17})_2O$. In addition to these products, two others are obtained from the aqueous solution by acidifying with acetic acid, when an oil separates which soon becomes partially solid, and by crystallizing this product from warm alcohol, a compound of the formula $C_{20}H_{34}O_3$ is obtained in large rhombic plates, melting at about 127°, and distilling unchanged at 295° C. This body manifests very feeble acid properties. The alcoholic mother-liquor furnishes a relatively much smaller quantity of a very viscid uncrystallizable compound of the formula $C_{12}H_{22}O_3$, which appears to be the homologue of ethylic acetoacetate; it possesses marked acid properties.

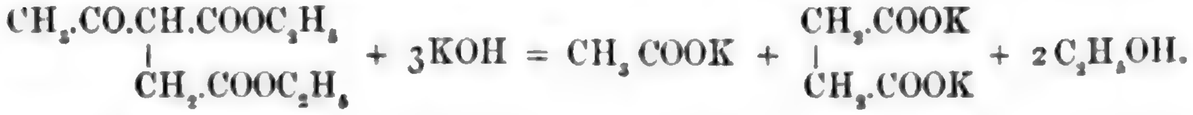
None of these various products appear to have been investigated, and even the composition of some of them is doubtful, as the method employed in effecting their purification can scarcely be regarded as efficient. There can be no question, however, that the reaction is far less simple than in the case of ethylic acetate.

(1831) **Dehydracetic Acid**: $C_8H_8O_4$.—This acid was originally obtained by Geuther by heating ethylic acetosodacetate in a current of carbonic anhydride or hydrochloric acid gas (*Zeits. Chem.*, 1866, 8), but only a very small quantity is produced in this manner. It is obtained as a bye-product in the preparation of ethylic acetoacetate (1824), which is in great part converted into ethylic acetate and dehydracetic acid by heating for three hours in sealed tubes at 230°—250° (446°—482° F.) (Conrad, *Deut. chem. Ges. Ber.*, vii. 688). According to Oppenheim and Precht (*ibid.*, ix. 323, 1099), ethylic acetoacetate furnishes nearly 25 per cent. of its weight of dehydracetic acid when passed through an iron tube heated to a temperature just below dull redness, a considerable amount of acetone being also produced.

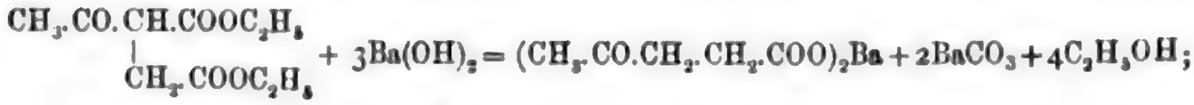
Dehydracetic acid crystallizes from a hot, aqueous solution in rhombic plates or needles, melting at 108°·5 (227°·3 F.); it boils at about 269° (516°·2 F.), but partially decomposes. It is difficultly soluble in cold, but readily in hot water; the solution has an acid reaction, and is coloured yellow to orange-red by ferric chloride according to the concentration. Dehydracetic acid is monobasic, furnishing a number of crystalline salts of the formula $C_8H_7MO_4$; its methylic salt crystallizes in four-sided prisms melting at 97° (195°·8 F.), the ethylic salt melting at 91°·6 (196°8 F.). According to Oppenheim and Precht, it is scarcely affected by the strongest hydrochloric, nitric or sulphuric acid, but is very readily decomposed by alkalies, yielding acetic and carbonic acids and acetone. On treatment with phosphoric pentachloride, it yields a crystalline chloride of the formula $C_8H_6O_2Cl_2$, and is thus shown to contain the HO group twice. Crystalline monochloro- and monobromo-derivatives are obtained in small quantity by the action of bromine on the acid. It appears to lose oxygen when submitted to the action of nascent hydrogen. On evaporating its solution in aqueous ammonia, it is converted into the amide $C_8H_7O_3.NH_2$, and the corresponding anilide, $C_8H_7O_3.NH.C_6H_5$ is produced on heating it with aniline.

(1832) ETHYLIC ETHOXYACETOETHOXYACETATE: $C_{10}H_{18}O_5$.—This compound is formed on treating ethylic ethoxyacetate, $CH_2(OC_2H_5).COOC_2H_5$, with sodium, &c., and bears to it precisely the same relation that ethylic acetoacetate bears; to ethylic acetate. It boils at about 245° (473° F.). It yields a violet coloration with ferric chloride; dissolves sodium; and is decomposed by acids with evolution of carbonic anhydride, and by alkalies with formation of alcohol and the corresponding ethoxyacetate (Geuther; Conrad, *ibid.*, xii. 58).

(1833) α-ACETOPROPIONIC ACID; *Lævulinic Acid*: $C_5H_8O_3 = CH_3.CO.CH_2.CH_2.COOH$.—By decomposing ethylic acetosuccinate, prepared by the action of ethylic monochloracetate on ethylic acetosodacetate, with a concentrated alcoholic solution of potassic hydrate, or by hydrochloric acid, potassic succinate and acetate are produced; but if baric hydrate be employed, baric acetopropionate and carbonate are formed. Thus:



$$\begin{array}{l}CH_3.CO.CH.COOC_2H_5\\ \qquad\qquad | \\ \qquad\quad CH_2.COOC_2H_5\end{array} + 3KOH = CH_3.COOK + \begin{array}{l}CH_2.COOK\\ | \\ CH_2.COOK\end{array} + 2C_2H_5OH.$$



$$\begin{array}{l}CH_3.CO.CH.COOC_2H_5\\ \qquad\qquad | \\ \qquad\quad CH_2.COOC_2H_5\end{array} + 3Ba(OH)_2 = (CH_3.CO.CH_2.CH_2.COO)_2Ba + 2BaCO_3 + 4C_2H_5OH;$$

The acid thus obtained is identical with the so-called lævulinic acid produced by heating lævulose (q. v.) with dilute sulphuric acid (Conrad, *Ann. Chem. Pharm.*, clxxxviii. 217; *Deut. chem. Ges. Ber.*, xi. 2177).

(1834) RICINOLEIC ACID: $C_{18}H_{34}O_3$.—As glyceric salt, this acid forms the chief constituent of castor oil—the oil expressed from the seeds of *Ricinus communis.* The acid itself is a colourless oil, which solidifies to a granular mass when cooled a few degrees below 0° (32·° F.); it furnishes a number of metallic salts of the form $C_{18}H_{33}MO_3$, which may be crystallized from alcohol or ether. Neither the acid nor its salts oxidize on exposure to the air. Like oleic acid, it may be converted by the action of nitrous acid into a crystalline isomeride melting at 50° (122° F.). When distilled alone ricinoleic acid undergoes decomposition into normal heptaldehyde (1645) and other products. Castor oil is similarly changed, and when distilled under much reduced pressure yields about 18 per cent. of its weight of this aldehyde together with about 10 per cent. of an acid of the acrylic series of the formula $C_{11}H_{20}O_2$ (Krafft. *Deut. chem. Ges. Ber*,, x. 2034; Becker, *ibid.* xi. 1412). Heptaldehyde is also obtained on subjecting the alkali-metal salts of ricinoleic acid to dry distillation, but if sodic ricinoleate be distilled with sodic hydrate, methylhexylcarbinol and methylhexylketone are produced in varying relative proportions depending upon the amount of hydrate and the temperature employed; the residue contains sodic sebate, $C_{10}H_{16}Na_2O_4$ (comp. Neison, *Jour. Chem. Soc.* xxvii. 507, 837). By the action of hydriodic acid, ricinoleic acid is converted into an iodo-acid of the formula $C_{18}H_{33}IO_2$; this combines with two atoms of bromine, and when submitted to the action of nascent hydrogen yields stearic acid, $C_{18}H_{36}O_2$ (Claus, *Deut. chem. Ges. Ber.*, ix. 1916).

Two of the atoms of oxygen in ricinoleic acid are undoubtedly present in the form COOH; the condition of the third is not yet ascertained, but from the behaviour of the acid on dry distillation being so similar to that of dieth-β-hydroxybutyric acid (1812) it would seem not improbable that it is present as OH. On this assumption the following appears to be the most probable formula of the acid:

$$(C_6H_{13})^{\alpha}.CH(OH).CH = CH.C_8H_{16}.COOH.$$

§ III. ACIDS OF THE C_nH_{2n} $(COOH)_2$ OR SUCCINIC SERIES.

The acids of the acetic series may be regarded as formed from the corresponding paraffins containing the same number of carbon atoms by the conversion by oxidation of the group CH_3 into $C(OH)_3$, and the removal of the elements of a single molecule of water from this group; in like manner, the acids of the oxalic or succinic series may be regarded as derived from the corresponding acids of the acetic series by the repetition of these operations, or, in other words, as formed from the corresponding paraffins by the conversion of two CH_3 groups into carboxyl.

(1835) The following is a list of the acids at present known:

			M.P. °C.
$C_2H_2O_4$	Oxalic acid	$COOH.COOH$	
$C_3H_4O_4$	Malonic acid	$CH_2(COOH)_2$	140
$C_4H_6O_4$	Succinic acid	$CH_2(COOH).CH_2(COOH)$	180·5
	Methylmalonic acid	$CH_3.CH(COOH)_2$	130
$C_5H_8O_4$	Propane-*a*-dicarboxylic acid	$CH_2(COOH).CH_2.CH_2(COOH)$	98
	Methylsuccinic or pyrotartaric acid	$CH_3.CH(COOH).CH_2(COOH)$	112
	Ethylmalonic acid	$C_2H_5.CH(COOH)_2$	112
	Dimethylmalonic acid	$(CH_3)_2C(COOH)_2$	170
$C_6H_{10}O_4$	Tetrane-*a*-dicarboxylic or adipic acid	$CH_2(COOH).(CH_2)_2.CH_2(COOH)$.	148
	a-Dimethylsuccinic acid	$CH_3.CH(COOH).CH(CH_3)(COOH)$	166
	Ethylsuccinic acid	$C_2H_5.CH(COOH).CH_2(COOH)$	98
	Methylpropane-*a*-dicarboxylic acid	$CH_3.CH(COOH).CH_2.CH_2(COOH)$	76
$C_7H_{12}O_4$	Pentane-*a*-dicarboxylic acid	$CH_2(COOH).(CH_2)_3.CH_2(COOH)$	103
	Pimelic acid		114
$C_8H_{14}O_4$	Hexane-*a*-dicarboxylic or suberic acid	$CH_2(COOH).(CH_2)_4.CH_2(COOH)$	140
	Tetramethylsuccinic acid	$(CH_3)_2C(COOH).C(CH_3)_2(COOH)$	95
	Heptane-*a*-dicarboxylic or azelaic acid	$CH_2(COOH).(CH_2)_5.CH_2(COOH)$.	106
	Octane-*a*-dicarboxylic or sebacic acid	$CH_2(COOH).(CH_2)_6.CH_2(COOH)$	127
	Brassylic acid	$C_9H_{18}(COOH)_2$	109
	Rocellic acid	$C_{15}H_{30}(COOH)_2$	132

(1836) METHODS OF FORMATION.—The following methods are all of more or less general application.

1. By oxidation of paraffins. No method of directly converting paraffins into the corresponding acids of the succinic series is known, but oxalic and succinic acids and other acids of the series are frequently produced on oxidizing the higher paraffins.

2. By oxidation of acids of the acetic series, as in the formation of succinic acid from butyric acid on heating it with nitric acid:

$$CH_3.CH_2.CH_2.COOH + 3(O + OH_2) = C(OH)_3.CH_2.CH_2.COOH + 3OH_2;$$
$$C(OH)_3.CH_2.CH_2.COOH = COOH.CH_2.CH_2.COOH + OH_2.$$

3. By oxidation of the corresponding glycols:

$$CH_2(OH).C_nH_{2n}.CH_2(OH) + 4(O + OH_2) = COOH.C_nH_{2n}.COOH + 6OH_2.$$

4. By converting dihaloid derivatives of paraffins into the corresponding dicyano-derivatives, and treating these latter with water and an alkali or mineral acid:

$$\underset{\text{α-Dibromopropane.}}{CH_2Br.CH_2.CH_2Br} + 2KCN = \underset{\text{α-Dicyanopropane.}}{CH_2(CN).CH_2.CH_2(CN)} + 2KBr;$$

$$\underset{\text{α-Dicyanopropane.}}{CN.CH_2.CH_2.CH_2.CN} + 6OH_2 = C(OH)_3.CH_2.CH_2.CH_2.C(OH)_3 + 2NH_3;$$

$$C(OH)_3.CH_2.CH_2.CH_2.C(OH)_3 = \underset{\text{Propane-α-dicarboxylic acid.}}{COOH.CH_2.CH_2.CH_2.COOH} + 2OH_2.$$

In a similar manner, they are obtained from monohaloid derivatives of acids of the acetic series, by treating ethereal salts of these latter with a metallic cyanide, &c., thus:

$$\underset{\text{Ethylic chloracetate.}}{CH_2Cl.COOC_2H_5} + KCN = \underset{\text{Ethylic cyanacetate.}}{CH_2(CN).COOC_2H_5} + KCl.$$

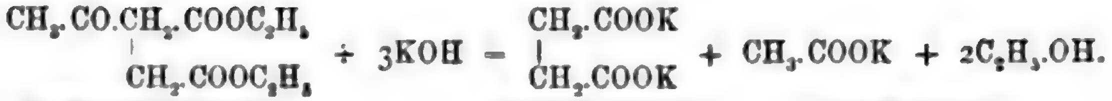
$$\underset{\text{Ethylic cyanacetate.}}{CN.CH_2.COOC_2H_5} + 3OH_2 = \underset{\text{Malonic acid.}}{COOH.CH_2.COOH} + NH_3 + C_2H_5OH.$$

Many dihaloid derivatives of paraffins and monohaloid derivatives of acids of the acetic series, however, are not available for the preparation of acids of the succinic series in this manner, as, instead of exchanging the halogen for the group CN, they lose the elements of a molecule of haloid acid.

5. By the action of metallic silver on ethereal salts of monohaloid derivatives of acids of the acetic series; *e.g.*:

$$\underset{\text{Ethylic α-iodopropionate.}}{2CH_3I.CH_2.COOC_2H_5} + 2Ag = 2AgI + \underset{\text{Ethylic adipate.}}{C_4H_8(COOC_2H_5)_2}.$$

6. By the decomposition of derivatives of ethylic acetoacetate of the form Ac.CH(C_nH_{2n}.COOEt).COOEt (comp. 1827, 1828), by means of a concentrated alcoholic solution of potassic hydrate or (?) concentrated hydrochloric acid:



$$\begin{matrix}CH_2.CO.CH_2.COOC_2H_5\\ |\\ CH_2.COOC_2H_5\end{matrix} + 3KOH = \begin{matrix}CH_2.COOK\\ |\\ CH_2.COOK\end{matrix} + CH_3.COOK + 2C_2H_5.OH.$$

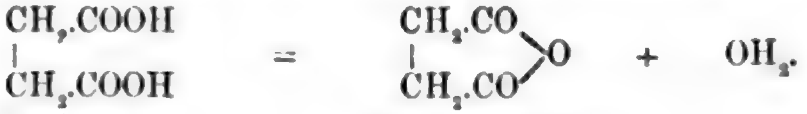
Ethylic acetosuccinate. Potassic succinate. Potassic acetate.

(1837) *Properties.*—The acids of the succinic series are all crystalline bodies. In their chemical behaviour they in many respects resemble the acids of the acetic series, but are less stable, being either partially or entirely decomposed on distillation: those in which the two carboxyl groups are associated with the *same* carbon atom being resolved into carbonic anhydride and an acid of the acetic series:

$$CH_3.CH(COOH)_2 = CH_3.CH_2.COOH + CO_2;$$

Isosuccinic acid. Propionic acid.

whilst those in which the two carboxyl groups are associated with *contiguous* carbon atoms, furnish corresponding anhydrides:



$$\begin{matrix}CH_2.COOH\\ |\\ CH_2.COOH\end{matrix} = \begin{matrix}CH_2.CO\\ |\\ CH_2.CO\end{matrix}\!\!>O + OH_2.$$

Succinic acid. Succinic anhydride.

Those in which the carboxyls are associated with non-contiguous carbon atoms have been little investigated, but they do not appear to furnish corresponding anhydrides, at least in any quantity, being apparently, for the most part, unchanged on distillation, or undergoing decomposition in other ways.

(1838) Oxalic Acid: $C_2H_2O_4 = (COOH)_2$.—This acid is found abundantly as a potassic salt in the leaves of the wood sorrel, *Oxalis acetosella*, and in many other species of *oxalis* and *rumex*; it also exists as a sodic salt in *salicornia* and *salsola*, and as calcic oxalate in a great number of, if not in all plants, the so-called 'raphides' being generally crystallized calcic oxalate. It is also of frequent occurrence as calcic salt in the animal kingdom, being found in the urine and in urinary deposits.

It may be formed—1, as sodic salt, by the direct union of carbonic anhydride with metallic sodium (Drechsel, *Zeits. Chem.*, 1868, 120), which takes place at about the boiling point of mercury: $2Na+CO_2=C_2O_4Na_2$; 2, also as sodic salt, by carefully heating sodic formate (Erlenmeyer and Gütschow): $2H.COONa=H_2+C_2O_4Na_2$; 3, as ammonic salt, together with other products, by the gradual decomposition of an aqueous solution of cyanogen: $C_2N_2+4OH_2=C_2O_4(NH_4)_2$; the conversion of cyanogen into oxalic acid is readily completely effected by digesting it with a dilute solution of a mineral acid or of an alkali; 4, by oxidation of a very large number of carbon compounds, especially oxygenated bodies, such as glycerol, tartaric acid, sugar, starch and cellulose, by means of oxidizing agents, such as nitric acid and potassic hydrate. Oxalic acid was formerly prepared on the large scale by oxidizing sugar or starch with nitric acid, but it is now almost entirely obtained by heating sawdust with a mixture of potassic and sodic hydrate, which is found to answer as well as potassic hydrate alone, although sodic hydrate is said not to furnish satisfactory results.

According to Schunck, Angus Smith, and Roscoe (*Brit. Assoc. Report*, 1861, p. 120), the following method is employed by Messrs. Roberts, Dale and Co.:—A concentrated solution of the two hydrates of sp. gr. 1·35 is prepared containing two molecular proportions of sodic hydrate to one of potassic hydrate, and into this sawdust is introduced so as to form a stiff paste. The pasty mass is placed in thick layers upon heated iron plates, and stirred constantly whilst the temperature is gradually raised. At first water escapes freely; as the decomposition advances the mass swells up and disengages an inflammable gas, containing hydrogen and methane. The temperature is maintained at a point between 200° and 250° (392° and 482° F.) for a couple of hours, when a dark brown mass, entirely soluble in water, is obtained. The exact nature of this mixture has not been ascertained. At this stage, however, it contains only from one to four per cent. of oxalic acid and a trace of formic, but no acetic acid; the application of heat to the mass is therefore continued for three or four hours longer, taking care to avoid charring: the mass becomes thoroughly dry, and finally contains from 28 to 30 per cent. of oxalic acid. Hydrogen appears to be given off continuously during the process, which is quite successful in closed vessels.

The grey mass thus procured is treated with water at 15° (59° F.) which dissolves out everything but the sparingly soluble sodic oxalate. The mother-liquors, after the separation of the sodic oxalate, are boiled down to dryness, and ignited to destroy organic matter; the residue is then rendered caustic, and after the addition of a suitable quantity of sodic hydrate used in preparing a fresh charge.

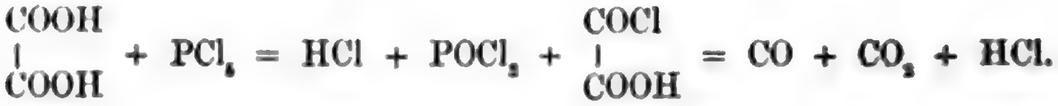
The sodic oxalate is decomposed by boiling with calcic hydrate, calcic oxalate being formed, which separates in the insoluble condition, whilst sodic hydrate enters into solution, and may be used over again. The calcic oxalate thus obtained is decomposed by means of sulphuric acid, and the liquor, decanted from the calcic sulphate, furnishes crystallized oxalic acid on evaporation. Sawdust treated by this method yields about half its weight of oxalic acid.

Thorn, who appears to have been unacquainted with the method adopted on the large scale, has made a number of experiments with a view to ascertain the most favourable conditions for the conversion of woody fibre into oxalic acid (*Journ. pr. Chem.*, 1873 [2], viii. 182). He finds that a considerable amount of the acid (equal to about 30 to 50 per cent. of the weight of the sawdust) may be obtained by the use of sodic hydrate alone. When potassic hydrate is employed alone, more is formed (about 85 per cent.) than with any mixture of the two hydrates if the mass be heated in a vessel of some depth; but if it be spread in a moderately thin layer on an iron plate, no advantage is gained by employing a mixture containing more than 40 pts. KOH to 60 pts. NaOH. Thus the following results were obtained on treating mixtures of 50 pts. pine sawdust (containing 15 per cent. hygroscopic moisture) and 100 pts. alkali for one to one and a half hours:

Proportion of KOH : NaOH.	Temperature. ° C.	No. of Experiments.	Percentage of oxalic acid.
0 : 100	200—220	2	33·14
10 : 90	230	2	58·36
20 : 80	240—250	4	74·76
30 : 70	240—250	3	76·77
40 : 60	240—250	6	80·57
60 : 40	240—250	6	80·08
80 : 20	245	4	81·24
100 : 0	240—250	6	81·23

Soft woods, such as fir, pine and poplar, gave a larger amount of acid than hard woods, such as beech and oak.

Oxalic acid crystallizes in colourless transparent monoclinic prisms of the composition $C_2H_2O_4 + 2OH_2$, very soluble in water and alcohol; it is highly poisonous. It melts at 98° (208°·4 F.), and readily loses its water of crystallization if maintained at about this temperature; the anhydrous acid begins to sublime at a somewhat higher temperature, but is in great part decomposed into CO_2, CO and OH_2, a small quantity undergoing conversion into formic acid and carbonic anhydride (comp. p. 822). When heated with substances having an affinity for water, such as sulphuric acid, it is readily resolved into carbonic anhydride, carbonic oxide, and water. It is completely decomposed by the chlorides of phosphorus; thus:



$$\begin{matrix}COOH\\|\\COOH\end{matrix} + PCl_5 = HCl + POCl_3 + \begin{matrix}COCl\\|\\COOH\end{matrix} = CO + CO_2 + HCl.$$

Chlorine and bromine have no action on the anhydrous acid, but in presence of water they oxidize it to carbonic acid. It is only slowly attacked even by boiling nitric acid, but most other oxidising agents rapidly convert it into carbonic acid; it is, however, a less powerful reducing agent than formic acid, separating the metal from auric, but not from platinic chloride.

Metallic Oxalates.—Oxalic acid furnishes *acid salts*, such as hydric potassic oxalate (potassic binoxalate, salt of sorrel), KHC_2O_4, and hydric baric oxalate, $Ba(HC_2O_4)_2 + 4OH_2$; a large number of *normal salts*, such as dipotassic oxalate, $K_2C_2O_4$, calcic oxalate, CaC_2O_4, &c.; numerous *mixed* (so-called double) *salts*, such as dipotassic cupric oxalate, $K_2Cu(C_2O_4)_2$, and a few, such as the plumbic oxalato-nitrate $C_2O_4(PbNO_3)_2$. The so-called quadroxalates and basic oxalates may be formulated as derivatives of the ortho-acid or acidhydrol $C(OH)_3.C(OH)_3$, as which we may regard crystallized oxalic acid; thus, the "basic" plumbic oxalate, $PbC_2O_4 . 2PbO = Pb_3C_2O_6$, may be regarded as the normal salt of this acid, while the hyperacid oxalate, $C_2HKO_4.C_2H_2O_4.2OH_2$, may be represented by the formula $C(OH)_3.C(OH)_2.O.C(OH)_2.COOK$.

The oxalates containing ammonium and the alkali metals are soluble in water, but most of the others are only very slightly soluble, or are insoluble in water, although readily dissolved by dilute acids. The oxalates of the alkali and alkaline earth metals are converted by ignition into carbonates without any appearance of charring, carbonic oxide being evolved; the oxalates of metals which have but a small attraction for oxygen furnish carbonic anhydride and a residue of the metal. The decomposition of argentic oxalate in this manner takes place so readily that it detonates when suddenly heated, whilst mercuric oxalate detonates violently on merely rubbing the dry salt.

Ethereal Oxalates.—The normal salts are best prepared by slow distillation of mixtures of the carbinols and dehydrated oxalic acid,* the product which always contains a certain amount of the corresponding ethereal formate being purified by fractional distillation; they are also formed on saturating these mixtures with hydrochloric acid gas, or by distilling them with sulphuric acid, and by the action of chlorides, bromides and iodides of hydrocarbon radicles on metallic oxalates.

Methylic oxalate, $C_2O_4(CH_3)_2$, crystallizes in glistening plates, melting at 51° (123°·8 F.), and boils at 162° (353°·6 F.); it is frequently employed in preparing pure methylic alcohol. The homologous compounds are liquid; *ethylic oxalate* boils at 186° (366°·8 F.); *propylic oxalate* at 210° (410° F.); *isobutylic oxalate* at 225° (437° F.); *isamylic oxalate* at 262° (503°·6 F.). *Benzylic oxalate*, $C_2O_4(CH_2.C_6H_5)_2$, obtained by the action of benzylic chloride on argentic oxalate crystallizes in brilliant white scales, melting at 80°·5 (176°·9 F.).

These salts are decomposed by water, and still more readily by alkalies, the latter forming crystalline metallic ethereal oxalates: thus, on adding an alcoholic solution of potassic hydrate to an alcoholic solution of ethylic oxalate, *potassic ethylic oxalate*, $COOK.COOC_2H_5$ is produced.† The corresponding acid ethereal oxalates formed on treating these metallic ethereal salts with acids are extremely unstable, and cannot be isolated; they are also produced on heating oxalic acid with carbinols. By treating the metallic ethereal salts with the chlorides of phosphorus they are converted into chlorides of the form $ClCO.COOC_nH_{2n+1}$, &c., potassic ethylic oxalate, for example, yielding the chloride $ClCO.COOC_2H_5$ when acted upon by phosphoric oxychloride (Henry, *Deut. Chem. Ges. Ber.*, iv. 598). According to v. Richter (*ibid.*, x. 2228), this chloride is more readily produced by the action of phosphoric pentachloride on ethylic oxalate, the corresponding bromide being formed when phosphoric pentabromide is employed. It is a colourless mobile liquid, boiling without decomposition at about 130° (267°·8 F.) (Richter); water and alcohol at once decompose it; by the continued action of phosphoric pentachloride it is converted into ethylic trichloracetate (Richter).

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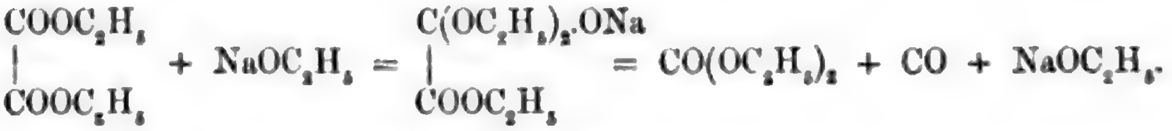
* Cahours and Demarcay have shown (*Compt. Rend.*, lxxxvi. 991) that this only holds good for primary carbinols, secondary and tertiary carbinols yielding corresponding olefines; and even primary carbinols of high molecular weight are similarly decomposed.

† The formation of these compounds is probably preceded by that of a compound of the ethereal oxalate with the metallic or ethereal hydrate, for Salomon has observed (*Deut. chem. Ges. Ber.*, viii. 1509) that when ethylic oxalate is treated with a solution of potassic methylate in methylic alcohol the product consists of potassic methylic oxalate; it may be supposed that the group $COOC_2H_5$ combines with the methylate forming $C(OCH_3)(OC_2H_5)(OK)$, and that C_2H_5OK is subsequently split off. According to Weddige (*Jour. pr. Chem.* [2] xii. 434) a similar change, but of the reverse order, takes place on treating *methylic* oxalate with a solution of ammonia in ethylic alcohol, whereby *ethylic* oxamate, $NH_2.CO.COOC_2H_5$, is formed. Frankland and Duppa have recommended the use of methylated spirit for the preparation of ethylic oxalate, and make no mention of the presence of methylic oxalate in the product (*Jour. Chem. Soc.*, xxii. 29); as the whole of the alcohol is not utilized it would be possible to explain the non-formation of the methylic salt in a similar manner.

Ethylic oxalate and its homologues are decomposed by sodium and potassium, being mainly converted into the corresponding carbonates with evolution of carbonic oxide: $C_2O_4(C_nH_{2n+1})_2 = CO_3(C_nH_{2n+1})_2 + CO$, comparatively small quantities of other products being formed. Geuther (*Zeits. Chem.*, 1868, 656), and Dittmar and Cranston (*Jour. Chem. Soc.*, 1869, xxii. 441) have shown that the action of sodic ethylate on ethylic oxalate is similar to that of sodium, and suggest that even when sodium is employed, the decomposition is really due to the action of the ethylate. According to the latter chemists, sodic ethylate gradually dissolves in ethylic oxalate with slight evolution of heat, forming a yellowish syrup, which sometimes gelatinizes on standing. If this product be gradually heated, a powerful reaction is observed to set in at about 80° (176° F.), large quantities of pure carbonic oxide being evolved, and the mass becomes darker and darker in colour, and at last almost black. On distilling the product from an oil-bath at a temperature not exceeding 200° (392° F.), a distillate is obtained containing ethylic carbonate, undecomposed ethylic oxalate, and a small quantity of ethylic alcohol, the last mentioned being always present, even when the most carefully dehydrated and dealcoholated substances are employed. The residue is black, and contains sodic oxalate, a small quantity of formate, and the sodic salts of a complex of organic acids not yet defined, but no carbonate if the proportion of ethylate used be not greater than about one-eighth of the weight of the oxalate. When the ethylate and oxalate are employed in simple molecular proportions, a considerable amount of sodic ethylic carbonate and ethylic ether are also formed by the action of the ethylate on the ethylic carbonate which is completely resolved into these two compounds by heating with the pure ethylate, and also furnishes them, together with carbonic oxide, when submitted to the action of sodium. Dittmar and Cranston found that a single mol. proportion of sodic ethylate, acting on an excess of ethylic oxalate, sufficed to decompose four mol. props. of the oxalate, producing three mol. props. of ethylic carbonate, and three of carbonic oxide, together with about ·4 mol. props. of alcohol. A single mol. prop. of potassic ethylate, however, was found capable of decomposing upwards of six mol. props. of ethylic oxalate, and to furnish no less than 1·6 mol. props. of alcohol to 6·2 mol. props. of ethylic carbonate. The principal decomposition, perhaps, takes place in the manner represented by the following equation:



$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + NaOC_2H_5 = \begin{array}{l} C(OC_2H_5)_2.ONa \\ | \\ COOC_2H_5 \end{array} = CO(OC_2H_5)_2 + CO + NaOC_2H_5.$$

According to Löwig, if ethylic oxalate be agitated with sodium amalgam, a product is obtained consisting of sodic oxalate and at least one other sodic salt, together with a fermentable sugar and the ethylic salt of a tribasic acid of the formula $C_5H_6O_8$, which he terms desoxalic or racemocarbonic acid. Brunner

(*Deut. chem. Ges. Ber.*, iii. 974), however, has failed in obtaining the sugar, and states that desoxalic acid (q.v.) has the formula $C_6H_8O_9$.

On treating an alcoholic solution of ethylic oxalate with sodium amalgam, salts of glycolic and tartaric acid are produced (Debus).

(1839) METHANEDICARBOXYLIC OR MALONIC ACID: $C_3H_4O_4 = CH_2(COOH)_2$.—This acid was originally obtained by Dessaignes by oxidation of malic acid. It may be formed, 1. from cyanacetic acid (1768); 2. by heating so-called barbituric acid, a uric acid derivative, with a solution of potassic hydrate; and 3. by boiling ethylic *a*-chloracrylate, $CHCl{=}CH.COOC_2H_5$, with a solution of baric hydrate (Pinner, *Deut. chem. Ges. Ber.*, viii. 963).

Malonic acid crystallizes in large flat triclinic prisms, easily soluble in water and alcohol; it melts at 140° (284° F.), and when heated at about 150° (302° F.) decomposes into acetic acid and carbonic anhydride.

Malonates.—Both the acid and normal salts of malonic acid, excepting those containing alkali metals, are sparingly soluble in water; the baric salt, $C_3H_2O_4Ba + 2OH_2$, is one of the most characteristic, crystallizing in aggregates of small thick prisms: it loses one of its mols. of water at 100° (212° F.), but the second is not expelled below 150° (302° F.) (comp. Finkelstein, *Ann. Chem. Phar.*, cxxxiii. 338).

(1840) ETHANEDICARBOXYLIC ACIDS: $C_4H_6O_4 = C_2H_4(COOH)_2$.—Only two dicarboxylic acids can be derived from ethane, and both are known—viz., succinic and isosuccinic acid.

(1841) SUCCINIC OR ETHANE-*a*-DICARBOXYLIC ACID, $COOH.CH_2.CH_2.COOH$, has been long known as a product of the distillation of amber (*succinum*), being mentioned by Agricola under the name of "volatile salt of amber" as early as 1657. It appears to be very widely distributed, having been found not only in amber, but also in certain lignites, in turpentine, in the juice of unripe grapes (Brunner and Brandenburg, *Deut. chem. Ges. Ber.*, ix. 982) and of the plants *Artemisia absinthium*, *Chelidonium majus* and *Lactuca virosa*; also in the animal organism, as in the thymoid gland of the calf, the spleen of the ox (Gorup-Besanez), in certain pathological exudations (Heintz), and in human urine after eating asparagus (Hilger, *Ann. Chem. Pharm.*, clxxi. 208).

Succinic acid may be obtained by the following reactions, among others:

1. By heating *a*-dicyanethane (ethylenic cyanide, 1220), obtained by digesting *a*-dibromethane or ethylenic bromide with an alcoholic solution of potassic cyanide, with water and an alkali or mineral acid (Maxwell Simpson, *R. Soc. Pr.*, x. 574; *Phil. Trans.*, 1861, 61; (comp. Jungfleisch, *Bull. Soc. Chim.* [2], xix. 197; Nevole and Tcherniak, *ibid.* [2], xxx. 101). Erlenmeyer and Simpson have shown (*Ann. Chem. Pharm.*, cxlv. 365, 373) that *β*-dichlor-

ethane or ethylidenic chloride, $CH_3.CHCl_2$, also yields succinic acid when heated with potassic cyanide, &c.: β-dichlorethane is, however, only acted upon by the cyanide at a temperature above 150° (302° F.), and is probably converted into monochlorethylene, and this, perhaps, unites with hydrocyanic acid, forming α-cyanochlorethane, $CH_2Cl.CH_2.CN$, which is subsequently converted into α-dicyanethane.

2. By heating α-iodopropionic acid with an aqueous solution of potassic cyanide, and digesting the product with a solution of potassic hydrate (v. Richter, *Zeits. Chem.*, 1868, 449).

3. By oxidation of higher terms of the paraffin series, of butyric acid and many of its homologues, and of many other carbon compounds. According to Erlenmeyer, Sigel and Belli (*Ann. Chem. Pharm.*, clxxx. 207), butyric acid is converted into succinic and carbonic acid and water by oxidation with nitric acid, the carbonic acid being probably the product of the further oxidation of the succinic acid; normal caproic acid yields succinic and acetic acid. In neither case is oxalic acid produced. The amount of succinic acid obtained from butyric acid is very small, but caproic acid furnishes about 50 per cent. of the quantity which can be formed by its resolution into succinic and acetic acid.

4. In small quantity by heating bromacetic acid with finely-divided silver at 130° (266° F.) (Steiner, *Deut. chem. Ges. Ber.*, vii. 184).

5. By heating ethylic acetosuccinate (1827, 1833) with a concentrated alcoholic solution of potassic hydrate.

6. By heating monhydroxy- and dihydroxy-succinic acid (malic and tartaric acid) with hydriodic acid. It may be conveniently prepared by this method by digesting a mixture of tartaric acid and a small quantity of water with iodine in a retort, adding small pieces of phosphorus from time to time; the hydriodic acid acts on the tartaric acid, forming succinic acid, water and iodine, but the iodine is no sooner liberated than it is reconverted into hydriodic acid, which then reduces a further quantity of tartaric acid.

7. By the combination of maleic and fumaric acid with nascent hydrogen.

8. As a product of fermentation. Succinic acid is a constant product of the fermentation of sugar by yeast, the amount obtained varying from about ·5 to ·7 per cent. of the weight of the sugar (Pasteur, *Ann. Chim. Phys.*, 1860 [3], lviii. 323). It is also formed in the conversion of alcohol into acetic acid under the influence of the *Mycoderma aceti* (Pasteur). Calcic malate furnishes nearly one-third its weight of succinic acid, and the acid may be advantageously prepared by fermenting the crude calcic malate obtained by neutralizing the expressed juice of mountain ash berries (*Sorbus Aucuparia*) with calcic carbonate: usually the product consists of a mixture of calcic acetate and malate, carbonic anhydride being evolved, but the formation of calcic lactate has often been observed, and it frequently happens that hydrogen is evolved, in which case calcic butyrate is also formed. The common practice is to add yeast or decayed cheese to initiate fermentation, and doubtless the formation of these various products is in a great measure to be ascribed to the presence of a variety of ferments. Fitz, in fact, has found (*Deut. chem. Ges. Ber.*, xi., 1890) that if a solution of calcic malate, to which small quantities of the necessary mineral salts have been added, be fermented by means of a *Bacillus* having the form of short thin rods, a mixture is obtained consisting of calcic acetate and succinate almost in the proportions required by the equation $3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + OH_2$; whereas, when a short cylindrical *Bacillus* was employed, he obtained a mixture of calcic propionate and acetate, 53·6 grams of malic acid giving about 18 grams propionic acid, 6 grams acetic acid and only ·07 grams succinic acid, together with 5 grams ethylic alcohol. According to the same observer, erythrol yields an amount of butyric and succinic acid on fermentation

almost equal to that required if two mols. are converted into a single mol. of each of these acids. Very small quantities of succinic acid are formed on fermentation of mannitol and citric acid (Fitz). Asparagine, and maleic, fumaric and aconitic acids also yield succinic acid on fermentation.

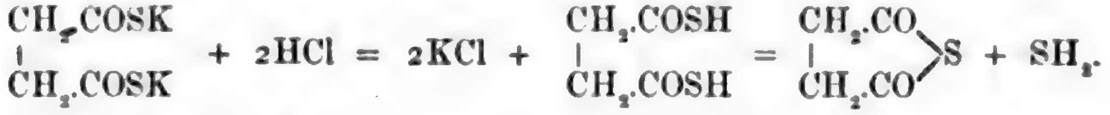
Succinic acid crystallizes in rhombic or hexagonal plates belonging to the monoclinic system, soluble in about 6 pts. of water at 18° (64°·4 F.) (comp. Bourgoin, *ibid.*, vii. 187); it is less soluble in alcohol, and almost insoluble in ether. It melts at 180°·5 (356°·9 F.), but if heated in an open tube, or on a flat surface, it sublimes considerably below this temperature, giving off fumes productive of violent coughing if inhaled; it boils at about 235° (455° F.), being resolved into succinic anhydride and water. It is a body of very considerable stability, being but slowly and imperfectly acted upon by most oxidizing agents: it may, however, be completely converted into carbonic acid and water by prolonged heating with nitric acid of sp. gr. 1·4 at 160°—180° (320°—356° F.) (Erlenmeyer, Sigel and Belli). It is not altered even by heating with concentrated sulphuric acid; but phosphoric anhydride converts it into succinic anhydride. When carefully fused with potassic hydrate, it yields a mixture of propionate and carbonate; according to Seekamp (*Ann. Chem. Pharm.* cxxxiii. 253), a similar decomposition takes place on exposing a solution of uranic succinate to sunlight. On electrolyzing a concentrated solution of sodic succinate, hydrogen is evolved at the negative, and a mixture of ethylene and carbonic anhydride at the positive pole (Kekulé).

Succinates.—The metallic derivatives of succinic acid, with the exception of magnesic succinate and the ammonic and alkali-metal salts, which are easily soluble, are sparingly soluble in water. *Calcic succinate*, which is one of the most characteristic, is gradually deposited in small needles of the composition $C_4H_4O_4Ca + 3OH_2$ on mixing cold concentrated solutions of calcic chloride and sodic succinate; but if the solutions are mixed hot, a precipitate is immediately formed of the composition $C_4H_4O_4Ca + OH_2$. Ferric chloride added to a solution of a succinate at once produces a reddish-brown precipitate of a basic salt.

Ethereal salts of succinic acid are readily obtained by the ordinary methods. Ethylic succinate, $C_4H_4O_4(C_2H_5)_2$, is an oily liquid boiling at about 217° (422°·6 F.).

(1842) SUCCINIC ANHYDRIDE: $C_4H_4O_3$.—This compound is formed on distilling succinic acid alone, and also on heating it with phosphoric pentoxide or pentachloride, or with acetic chloride, acetic anhydride or succinic chloride (Anschütz, *Deut. chem. Ges. Ber.*, x. 325, 1881); it is usually prepared by the aid of phosphoric pentachloride. Succinic anhydride may be crystallized from anhydrous alcohol apparently without change; boiling water reconverts it into the acid. It melts at 120° (248° F.), and boils at about 250° (482° F.). By distillation with phosphoric pentachloride it is converted into *succinic chloride*, $C_2H_4(COCl)_2$. This compound crystallizes when cooled to 0° (32° F.), and boils at about 190° (374° F.); it is readily decomposed by water and by alcohol. By gradually mixing succinic anhydride with baric peroxide and a little water, a solution is obtained having powerful oxidizing properties, and which is decomposed on boiling with evolution of oxygen and formation of baric succinate (Brodie, *Phil. Trans.*, 1863, 417).

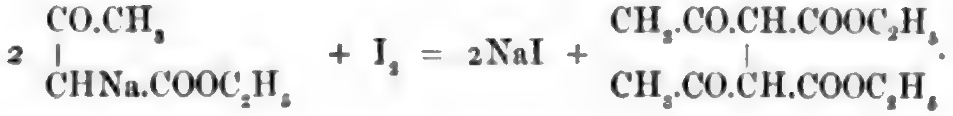
(1843) Thio-derivatives of Succinic Acid.—By heating phenylic succinate, $C_2H_4(COOC_6H_5)_2$, prepared by the action of succinic chloride on phenol, with a solution of potassic sulphydrate in anhydrous alcohol, it is converted into phenol and the salt $C_2H_4(COSK)_2$. This salt crystallizes in white needles; it is extremely soluble in water, and also dissolves readily in alcohol and ether, but the solutions rapidly alter in contact with air; it is decomposed by acids in the following manner:



$$\begin{matrix} CH_2.COSK \\ | \\ CH_2.COSK \end{matrix} + 2HCl = 2KCl + \begin{matrix} CH_2.COSH \\ | \\ CH_2.COSH \end{matrix} = \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>\!S + SH_2.$$

The compound $C_4H_4O_2S$ is crystalline, and very soluble in water, alcohol and ether; it has an acid reaction, and its solution yields precipitates with a number of metallic salts (Weselsky, *ibid.*, ii. 518).

(1844) Ethylic diacetosuccinate: $C_8H_8O_6(C_2H_5)_2$.—This compound is formed by the action of iodine on ethylic acetosodacetate (Rügheimer, *ibid.*, vii. 892):

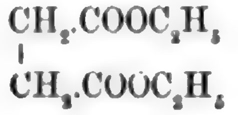


$$2\begin{matrix} CO.CH_3 \\ | \\ CHNa.COOC_2H_5 \end{matrix} + I_2 = 2NaI + \begin{matrix} CH_3.CO.CH.COOC_2H_5 \\ | \\ CH_3.CO.CH.COOC_2H_5 \end{matrix}.$$

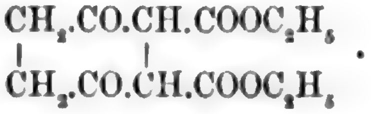
It crystallizes in rhombic plates, very soluble in alcohol, ether, and benzene; it melts at about 77° (170°·6 F.), undergoing partial decomposition. When boiled with dilute sulphuric acid, it yields ethylic alcohol and the ethylic salt of carbuvic acid: $C_8H_8O_6(C_2H_5)_2 + OH_2 = C_2H_5.OH + C_8H_9O_6(C_2H_5) = C_9H_7O_5(C_2H_5) + OH_2$, together with carbuvic acid, $C_8H_8O_5$, and an acid derived from carbuvic acid by the withdrawal of the elements of a molecule of carbonic anhydride: $C_8H_8O_5 - CO_2 = C_7H_8O_3$, this latter acid being identical with the uvic acid obtained on boiling acetoformic acid with a solution of baric hydrate (1820; Harrow, *Jour. Chem. Soc. Trans.*, 1878, 425).

(1845) Action of Alkali Metals on Ethylic Succinate.—Fehling in 1844 first studied the action of alkali metals on ethylic succinate, and obtained a product of the empirical formula $C_6H_4O_3$. Geuther subsequently suggested that this compound probably stood in the same relation to the parent substance as ethylic acetoacetate to ethylic acetate, a prediction which Hermann has since confirmed. According to Hermann (*Inaug. Dis.*, Tübingen, 1875; *Deut. chem. Ges. Ber.*, viii. 1039; x. 107, 646; comp. Remsen, *ibid.*, viii. 1408, ix. 8) potassium dissolves in ethylic succinate with evolution of hydrogen and considerable development of heat; when the amount of metal added is equal to from one-fifteenth to one-tenth of the weight of the succinate, a brown-red sticky mass is obtained, and further action becomes almost impossible. It is not advisable to heat on the water-bath, as this causes decomposition, but if two or three volumes of benzene be added and the mixture heated gently, a considerable further quantity of potassium can be dissolved; the entire amount added should not, however, exceed one-sixth of the weight of the succinate. The solid product is separated as far as possible from the liquid by filtration under reduced pressure, and is then decomposed with highly dilute hydrochloric acid; a yellowish coherent mass of the consistency of very soft butter is thus obtained, which may be purified by pressing between folds of porous paper, washing with cold alcohol, crystallizing from boiling alcohol, washing with water, and finally recrystallizing from ether. Sodium acts on ethylic succinate less violently than potassium, but ultimately furnishes the same compound; on exposure to air, the immediate product of the reaction forms a pale yellow pulverulent mass, and on this account sodium is preferable to potassium notwithstanding the slowness with which it acts.

Ethylic succinosuccinate as, for want of a better name, the product may be termed, appears to bear the relation to ethylic succinate indicated by the following formula:



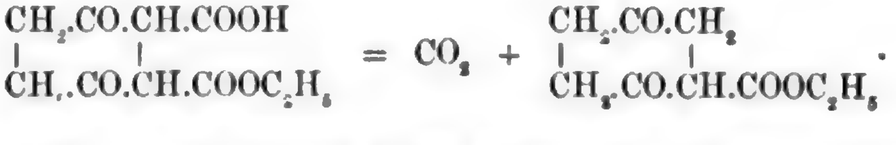
$$\begin{array}{l} CH_2.COOC_2H_5 \\ | \\ CH_2.COOC_2H_5 \end{array}$$



$$\begin{array}{l} CH_2.CO.CH.COOC_2H_5 \\ |\qquad\quad | \\ CH_2.CO.CH.COOC_2H_5 \end{array} .$$

It crystallizes with considerable facility, separating from its solution in ether or benzene by slow evaporation in large well-formed, glistening, transparent, triclinic prisms; the crystals are of a very faint greenish colour, except in one direction, in which they exhibit a pale-blue colour. It is easily soluble in hot benzene, alcohol, or ether, but only slightly soluble in these liquids at the ordinary temperature; mere traces only are dissolved by boiling water, but it is readily soluble in alkalies, forming yellow solutions, from which it is reprecipitated unchanged by acids. Its solutions in neutral media exhibit an intense pale blue fluorescence, very similar to that of quinine solutions, but there are two well-marked minima in the spectrum of the emitted light, one near D, the other near F, whereas there is only a single minimum between D and E in the quinine spectrum. Ethylic succinosuccinate melts at 127° (260°·6 F.), and is decomposed at a slightly higher temperature. It dissolves sodium and potassium with evolution of hydrogen, forming metallic derivatives, which are also obtained on dissolving it in solutions of the hydroxides of these metals; other derivatives may be prepared from these by double decomposition with various metallic salts: thus, magnesic sulphate produces a deep yellow-coloured precipitate which acquires a carmine-red colour when freed from the excess of the precipitant by washing with hot water. The composition of these metallic derivatives has not yet been satisfactorily ascertained.

Ethylic succinosuccinate is readily decomposed in contact with alkalies, but the products vary according as the solution is preserved from contact with the air or not. In the former case, if the unaltered succinosuccinate be precipitated after about two hours by saturating the solution with carbonic anhydride, and the filtered liquid be acidulated with acetic acid, a crystalline precipitate is thrown down which appears to be the acid ethylic salt of succinosuccinic acid; this compound melts at 98° (208°·4 F.) with evolution of carbonic anhydride, being converted into ethylic succinopropionate:



$$\begin{array}{l} CH_2.CO.CH.COOH \\ |\qquad\quad | \\ CH_2.CO.CH.COOC_2H_5 \end{array} = CO_2 + \begin{array}{l} CH_2.CO.CH_2 \\ |\qquad\quad | \\ CH_2.CO.CH.COOC_2H_5 \end{array} .$$

On adding dilute sulphuric acid to the filtrate from the precipitate caused by acetic acid, a second precipitate is obtained, which probably consists of succinosuccinic acid. The filtrate from this precipitate contains a third product not yet isolated, but on distilling the residue which remains on evaporation. quinol (hydroquinone) or paradihydroxybenzene, $C_6H_4(OH)_2$, is obtained; and if a solution of ethylic succinosuccinate in alkali which has been preserved for a considerable time out of contact with the air be acidulated with sulphuric acid and then treated with a large excess of bromine, bromo-derivatives of quinone are obtained in large quantity.

If the alkaline solution of succinosuccinate be exposed to the air, the above described decomposition-products are formed together with others varying according to the length of exposure; if sulphuric acid be added when the liquid acquires a brown colour, a precipitate is obtained from which boiling water extracts an acid, crystallizing in brownish-yellow needles of the composition $C_6H_4O_2\ (COOH)_2$; this acid yields quinol on fusion with potassic hydrate.

Herrmann has also made the important observation that orthohydroxybenzoic or salicylic acid, $C_6H_4(OH)COOH$, is formed in no inconsiderable quantity on digesting ethylic succinate with an excess of sodium (? without heating) for a period of several weeks.

(1846) ISOSUCCINIC ACID; METHYLMALONIC OR ETHANE-β-DICARBOXYLIC ACID: $CH_3.CH\ (COOH)_2$.—This acid was first obtained by H. Müller from ethylic β-chloropropionate, $CH_3.CHCl.COOC_2H_5$, by digesting with potassic cyanide, &c. (*Jour. Chem. Soc.* [2] ii. 109), but the isomerism of the acid thus produced with ordinary succinic acid was first recognised by Wichelhaus (*Ann. Chem. Pharm., Sup.* vi. 281) and v. Richter (*Zeits. Chem.*, 1868, 451); it has since been studied by Byk (*Jour. pr. Chem.* [2] i. 19), Schmoeger, (*ibid.* [2] xiv. 77), and Krestownikoff (*Deut. chem. Ges. Ber.*, x. 409). See also Zublin (*ibid.* xii. 1112).

Isosuccinic acid forms colourless prismatic crystals much more soluble in water than succinic acid; it sublimes even below 100° (212° F.) in microscopic plates, and melts at 130° (266° F.), but it commences to decompose a few degrees above 100° (212° F.) and on distillation is completely resolved into carbonic anhydride and propionic acid; when rapidly heated on platinum foil, it emits irritating vapours like those of succinic acid.

The metallic isosuccinates are, for the most part, much more soluble than the corresponding succinates, and readily decompose when heated; the alkaline isosuccinates do not furnish a precipitate with ferric salts. Ethylic isosuccinate does not decompose even at a temperature of 350° (662° F.).

(1847) PROPANEDICARBOXYLIC ACIDS: $C_5H_8O_4 = C_3H_6\ (COOH)_2$. The four dibasic acids which theoretically can be derived from propane are all known:

Propane-α-dicarboxylic acid	$CH_2(COOH).CH_2.CH_2(COOH)$.
Methylsuccinic or pyrotartaric acid	$CH_3.CH(COOH).CH_2(COOH)$.
Dimethylmalonic acid	$(CH_3)_2C(COOH)_2$.
Ethylmalonic acid.	$CH_3.CH_2.CH(COOH)_2$.

Propane-α-dicarboxylic or *glutaric acid*, $CH_2(COOH).CH_2\ CH_2(COOH)$, may be prepared from the dibromopropane $CH_2Br.CH_2.CH_2Br$, by the ordinary method (Lermontoff, *Ann. Chem. Pharm.*, clxxxii. 341: Reboul, *Ann. Chim. Phys.* [5], xiv. 455); by saturating a concentrated aqueous solution of glutanic acid, $C_3H_5(OH)(COOH)_2$ with hydriodic acid (Dittmar, Markownikoff, *ibid.*); and by decomposing with a concentrated alcoholic solution of potassic hydrate the ethylic salt obtained by the action of ethylic α-iodopropionate, $CH_2I.CH_2.COOC_2H_5$, on ethylic acetosodacetate (Wislicenus and Limpach, *ibid.* cxcii. 128). It is extremely soluble in water, and only slightly less soluble in ether, but nevertheless crystallizes very readily in large transparent broad four-sided prisms, melting at 95°—98° (203°—208°·4 F.) If rapidly and strongly heated, it distils almost unchanged at 290° (554° F.); but if slowly distilled, it is partially resolved into the anhydride and water, passing over almost entirely below 285° (545° F.). The anhydride may be obtained by treating the silver salt of the acid with an ethereal solution of acetic chloride, distillation of the acid with phosphoric anhydride yielding unsatisfactory results; it crystallizes in small needles, melting at 57° (134°·6 F.), and boils with partial decomposition at 282°—285° (539°·6 —545° F.) (Markownikoff, *Deut. chem. Ges. Ber.*, x. 1103).

The most characteristic salt of this acid is the zincic salt, which is less soluble in hot than in cold water, so that if a cold solution of the acid be saturated with zincic carbonate and then warmed, this salt is deposited as a granular precipitate, which under the microscope is seen to consist of rectangular plates with re-entering angles at the opposite smaller sides of the quadrangle.

Methylsuccinic or *pyrotartaric acid*, $CH_3.CH(COOH).CH_2(COOH)$, is obtained by dry distillation of tartaric acid, especially if the latter be mixed with powdered pumice, or by heating it with concentrated hydrochloric acid at 180° (356° F.) (Geuther and Reimann, *Zeits. Chem.*, 1869, 318); by the action of heat on glyceric acid (Moldenhauer) and acetoformic acid; from β-dibromopropane or propylenic bromide, $CH_3.CHBr.CH_2Br$ (Maxwell-Simpson; comp. Lebedeff, *Ann. Chem. Pharm.*, clxxxii. 327); by the action of nascent hydrogen on citra-, ita- and mesaconic acid, the three isomeric acids of the formula $C_3H_4(COOH_2)$; by heating allylic iodide with potassic cyanide, and decomposing the resulting dicyanopropane by boiling with alkali: apparently the iodine is displaced by the group CN and at the same time a molecule of hydrocyanic acid is added on: $CH_2{=}CH.CH_2I + KCN + HCN = CH_3.CH(CN).CH_2(CN) + KI$ (Claus, *ibid.*, cxci. 37); by the action of a concentrated alcoholic solution of potassic hydrate on ethylic acetomethylsuccinate (1827; Kressner, *ibid.*, cxcii. 135); and lastly by fusing gamboge with potassic hydrate (Hlasiwetz and Barth, *ibid.*, cxxxviii. 68).

Methylsuccinic acid crystallizes in rhombic prisms, melting at 112° (233°·6 F.). If it be rapidly heated to its boiling point and distilled, it is completely resolved into water and methylsuccinic anhydride, $C_5H_6O_3$, a colourless liquid boiling at 245°; but if it be heated for some time at about 200° (392° F.), it is only partially decomposed in this manner, a small portion being resolved into carbonic anhydride and butyric acid (Claus, *Deut. chem. Ges. Ber.*, viii. 100). Methylsuccinic acid does not furnish propylene on electrolysis (Reboul and Bourgoin, *Compt. Rend.*, lxxxiv. 1231).

Dimethylmalonic acid, $(CH_3)_2C\,(COOH)_2$, prepared from dimethylbromacetic (bromisobutyric) acid, crystallizes in four-sided prisms, difficultly soluble in alcohol, and also less soluble in water than the isomeric acids. It sublimes at about 120° (248° F.) in white needles, and melts at about 170° (338° F.), being resolved into carbonic anhydride and dimethacetic acid. This acid is remarkably stable in presence of oxidizing agents, scarcely being affected by boiling with potassic dichromate and sulphuric acid or by evaporation with dilute nitric acid (Markownikoff, *Ann. Chem. Pharm.*, clxxxii. 336).

Ethylmalonic acid, $C_2H_5.CH(COOH)_2$, prepared by heating ethylic bromobutyrate with an alcoholic solution of potassic cyanide, &c., crystallizes in rhombic prisms melting at 112° (233°·6 F.); it decomposes into butyric acid and carbonic anhydride when heated at about 160° (320° F.) (Wislicenus and Urech, *ibid.*, cxlv. 93; Markownikoff, *ibid.*, clxxx. 329; comp. Conrad, *Deut. chem. Ges. Ber.*, xii. 751).

(1848) TETRANEDICARBOXYLIC ACIDS: $C_6H_{10}O_4=C_4H_8(COOH)_2$.—Only four of these acids are satisfactorily known, viz.:

Tetrane-*a*-dicarboxylic (adipic) acid . .	$CH_2(COOH).CH_2.CH_2.CH_2(COOH)$.
Methylpropane-*a*-dicarboxylic acid . . .	$CH_3.CH(COOH).CH_2.CH_2(COOH)$.
a-Dimethylsuccinic acid	$CH_3.CH(COOH).CH(COOH).CH_3$.
Ethylsuccinic acid	$C_2H_5.CH(COOH).CH_2(COOH)$.

Laurent first obtained adipic acid by oxidizing oleic acid with nitric acid, and it was subsequently prepared in a similar manner from various fatty substances, such as tallow, linseed oil, wax and spermaceti, and from the mixture of solid acids of the acetic series produced by saponifying cocoa-nut oil; other homologous acids are formed at the same time, however, from which it is difficult to separate. The acid thus produced is shown to be tetrane-*a*-dicarboxylic acid by the formation of an identical substance by the action of finely divided silver (prepared by reducing the precipitated chloride with pure zinc) on *a*-iodopropionic acid (Wislicenus, *Ann. Chem. Pharm.*, cxlix. 220):

$$2\ CH_2I.CH_2.COOH + 2Ag = 2AgI + CH_2(COOH).CH_2.CH_2.CH_2(COOH).$$

According to Crum-Brown, adipic acid is formed on reducing mucic acid, $C_4H_4(OH)_4(COOH)_2$, by heating it with hydriodic acid, and it is also produced by treating muconic and hydromuconic acids with sodium amalgam (Limpricht). It crystallizes in colourless glistening plates or prisms, melting at 148° (298°·4 F.), easily soluble in alcohol, ether, and hot water. Its ammonic salt crystallizes with great facility in large rhombic plates: a solution of this salt furnishes a crystalline precipitate with calcic chloride on heating; crystalline precipitates are also gradually formed on mixing it with zincic and cadmic sulphate, and it yields a brown-red precipitate with ferric chloride. According to Kachler (*ibid.*, clxiv. 79; clxvi. 320), an isomeride of adipic acid is formed on oxidizing camphorone.

a-Dimethylsuccinic acid is obtained by decomposing ethylic acetodimethylsuccinate (1826) with potassic hydrate, &c. (Hardtmuth, *ibid.*, cxcii. 142). It is a crystalline acid melting at 166° (330°·8 F.). The same acid is probably formed on treating β-bromopionic acid, $CH_3.CHBr.COOH$, with finely divided silver (Wislicenus, *Deut. chem. Ges. Ber.*, ii. 720); and by similarly treating β_2-dichloropropionic acid and reducing the resulting dichloro-acid of the formula $C_6H_8Cl_2O_4$ (Beckurts and Otto, *ibid.*, x. 1503).

Methylpropane-a-dicarboxylic acid, obtained by decomposing the ethylic salt formed from ethylic α-iodopropionate and ethylic acetosodmethacetate with potassic hydrate, melts at 76° (168°·8 F.).

Ethylsuccinic acid has been prepared by decomposing ethylic β-acetoethylsuccinate with potassic hydrate. It crystallizes in fine prisms, extremely soluble in water and alcohol, melting at 98° (208°·4 F.) (Huggenberg, *Ann. Chem. Pharm.*, cxcii. 146).

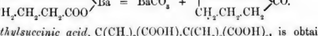
(1849) PENTANEDICARBOXYLIC ACIDS: $C_7H_{12}O_4 = C_5H_{10}(COOH)_2$.—Various chemists have stated that an acid of the formula $C_7H_{12}O_4$, which has been termed *pimelic acid*, is produced on oxidizing a number of fatty substances, but the descriptions given of the products are very discrepant, and the formation of such an acid is at present doubtful (comp. Kachler, *ibid.*, clxix. 168). Hlasiwetz and Grawbowski have found, however, that an acid of this formula is obtained on fusing camphoric acid (1687) with potassic hydrate, and their observations have been confirmed and extended by Kachler (*loc. cit.*). An apparently identical acid is obtained by acting on amylenic bromide with a mixture of potassic cyanide and hydrate (Bauer and Schuler, *Deut. chem. Ges. Ber.*, x. 2031). The acid from camphoric acid usually crystallizes in perfectly transparent hard crystalline crusts, but may be obtained in isolated triclinic prisms; it melts at 114° (237°·2 F.), and is converted into water and the corresponding anhydride on distillation. On adding calcic chloride to an ammoniacal solution of the acid and heating, the calcic salt is precipitated as a sandy crystalline powder; this behaviour is highly characteristic. From the manner in which it is decomposed on distillation, it would appear probable that the carboxyl groups in this acid are associated with contiguous carbon atoms.

An isomeric acid, which probably is the normal or pentane-*a*-dicarboxylic acid, $CH_2(COOH).(CH_2)_3.CH_2(COOH)$, is obtained by oxidizing suberone (1850) with nitric acid (Dale and Schorlemmer, *Jour. Chem. Soc.*, xxvii. 935), and by heating furonic acid, $C_7H_8O_5$, with hydriodic acid (Baeyer, *Deut. chem. Ges. Ber.*, x. 1358). It crystallizes in large transparent rectangular monoclinic plates, melting at 103° (217°·4); its most characteristic salt is also the calcic salt, which separates on boiling its concentrated solution as a granular flocculent precipitate, which redissolves on standing if the solution has not become too concentrated.

Diethylmalonic acid, $(C_2H_5)_2C(COOH)_2$, according to Conrad (*ibid.*, xii. 749), melts at 102° (233°·6 F.).

(1850) HEXANEDICARBOXYLIC ACIDS: $C_8H_{14}O_4 = C_6H_{12}(COOH)_2$.—Only two of these acids are known with certainty,—viz., *suberic acid*, which is probably the normal or hexane-*a*-dicarboxylic acid, and tetramethylsuccinic acid.

Suberic acid was first prepared by oxidizing cork (*suber*) by prolonged boiling with nitric acid, and was subsequently obtained as a product of the oxidation of a number of fatty substances and oils; it is best prepared from castor oil (comp. Arppe, *Ann. Chem. Pharm.*, cxxiv. 86). Suberic acid crystallizes in long needles or six-sided plates, sparing soulble in cold water and ether, but easily in boiling water; it melts at 140° (284°· F.), and sublimes between 150° and 160° (302°—320° F.), with partial decomposition, in slender needles. It yields a small quantity of hexane on distillation with excess of baric hydrate (Dale, *Jour. Chem. Soc.* xvii. 258); and on distillation with calcic hydrate it is converted into suberone, the corresponding ketone (Dale and Schorlemmer, *ibid.*, xxvii. 935; *ibid.*, *Trans.* 1879, 683):



$$\begin{matrix} CH_2.CH_2.CH_2.COO \\ | \\ CH_2.CH_2.CH_2.COO \end{matrix}\!\!>\!Ba = BaCO_3 + \begin{matrix} CH_2.CH_2.CH_2 \\ | \\ CH_2.CH_2.CH_2 \end{matrix}\!\!>\!CO.$$

Tetramethylsuccinic acid, $C(CH_3)_2(COOH).C(CH_2)_2(COOH)_2$, is obtained as ethylic salt on heating ethylic dimethylbromacetate (bromisobutyrate), $CBr(CH_3)_2.COOC_2H_5$, with finely divided silver. The acid itself crystallizes in small aggregates of quadratic plates, melting at 95° (203° F.); it is extremely soluble in alcohol, ether, and hot water. Diethylsuccinic acid has been prepared in a similar manner from ethylic bromobutyrate, but not yet described (Hell and Wittekind, *Deut. chem. Ges. Ber.* vii. 319).

(1851) AZELAIC ACID; *lepargylic* or *anchoic acid*, $C_9H_{16}O_4 = C_7H_{14}(COOH)_2$, is formed with other acids of the series on oxidation of many fatty substances and cork, and is the chief solid acid produced on boiling castor oil with nitric acid (Arppe; comp. Grote, *Ann. Chem. Pharm.*, cxxx., 207); it is also formed on oxidation of stearolic acid (comp. Limpach, *ibid.*, cxc. 294). It crystallizes in large lustrous plates or flattened needles, very sparingly soluble in cold water, but without difficulty in hot water, alcohol, and ether: it melts at 106° (222°·8 F.). When distilled with baric hydrate, it yields normal heptane (Dale and Schorlemmer, *Jour. Chem. Soc. Trans.*, 1879, 683). By heating butyrofuronic acid with hydriodic acid, an acid which appears to be the normal pimelic acid is produced; it melts at 118° (2448·4 F.) (Toennies, *Deut. chem. Ges. Ber.*, xii. 1200).

(1852) Sebacic or Sebic Acid; *Ipomæic acid*, $C_{10}H_{18}O_4 = C_8H_{16}(COOH)_2$, is formed in small quantity by the dry distillation of many fatty bodies, or by their oxidation with nitric acid, but is best prepared by heating the soap formed by treating castor oil with an excess of sodic hydrate (comp. Neison, *Jour. Chem. Soc.*, xxvii. 301; Witt, *Deut. chem. Ges. Ber.*, vii. 219). It crystallizes in long feathery needles or thin brilliant laminæ, soluble in 1500 parts of water at 10° (50° F.), or in 50 parts boiling water, and easily soluble in alcohol and ether; it melts at 127° (260° F.). When distilled with baric hydrate, it yields octane, and, among other products, cetylic alcohol, $C_{16}H_{33}.OH$, which itself furnishes sebacic acid on oxidation (Schorlemmer, *ibid.*, iii. 616). The sebates have been carefully examined by Neison (*loc. cit.*).

(1853) Brassylic Acid, $C_{11}H_{20}O_4 = C_9H_{18}(COOH)_2$, is said to be formed on oxidation of behenolic acid with nitric acid; it crystallizes in scales melting at 109° (228°·2 F.), and only slightly soluble even in boiling water.

(1854) Rocellic Acid, $C_{17}H_{32}O_4 = C_{15}H_{30}(COOH)_2$, an acid contained in the lichens *Rocella tinctoria* and *Lecanora tartarea*, crystallizes in colourless prisms melting at 132° (269°·6 F.); it is said to yield an anhydride on distillation.

(1855) Haloid Derivatives of the Acids of the Succinic Series.—Very few haloid derivatives have been prepared by the direct action of halogens on the acids of the succinic series; most of those which are known have been obtained by combining acids of the $C_nH_{2n-2}(COOH)_2$ series with haloid acids and halogens.

Malonic Acid Derivatives.—On treating an aqueous solution of malonic acid with bromine, chiefly bromo-derivatives of acetic acid are produced, but if the reacting substances are dissolved in chloroform, *dibromomalonic acid*, $CBr_2(COOH)_2$, is obtained; it crystallizes in needles melting at 127° (260°·6 F.) (Petrieff, *Deut. chem. Ges. Ber.*, vii. 400; viii. 730; xi. 414).

Succinic Acid Derivatives.—A monobromo- and two isomeric dibromo-derivatives of this acid are formed on heating it with bromine and water; the monobromo-acid being chiefly produced when a considerable amount of the latter is present (Kekulé, Carius). *Monobromosuccinic acid* is more easily prepared, however, by heating fumaric acid with a solution of hydrobromic acid saturated at 0° (32° F.); it crystallizes in hard glistening octahedra, melting at 159° (318°·2 F.), easily soluble in water; it is reconverted into fumaric acid by boiling with a moderately concentrated solution of hydrobromic acid (Fittig and Dorn, *Ann. Chem. Pharm.*, clxxxviii. 87).

Dibromosuccinic acid may also be obtained by combining fumaric acid with bromine, or bromomaleic acid with hydrobromic acid, and by heating succinic chloride with bromine and decomposing the product with water (Perkin and Duppa); it crystallizes in colourless prisms, only sparingly soluble in cold, but easily in hot water; it decomposes without fusing when heated above 200° (392° F.); when boiled with water, it is completely resolved into hydrobromic acid and bromomaleic acid, $C_2HBr(COOH)_2$ (Fittig and Petri, *ibid.*, cxcv, 56). *Isodibromosuccinic acid* is produced on combining maleic acid with bromine or bromofumaric acid with hydrobromic acid; it forms large transparent crystals, melting at 160° (320° F.), much more soluble in water than its isomeride; when heated with water, it yields bromofumaric acid. Both bromomaleic and bromofumaric acids combine with bromine forming the same *tribromosuccinic* acid; this crystallizes in bundles of small short prisms, melting at 137°

(278°·6 F.), extremely soluble in water; when boiled with water, it is resolved into hydrobromic acid, carbonic anhydride and dibromacrylic acid (Fittig and Petri, *loc. cit.*): $C_2HBr_3(COOH)_2 = CO_2 + HBr + C_2HBr_2.COOH$.

Isosuccinic Acid Derivatives.—Monobromisosuccinic acid is very readily obtained on heating isosuccinic acid with water at 100° (212° F.); it crystallizes in well-formed extremely deliquescent prisms (Byk, Schmoeger, *Jour. pr. Chem.* [2], xiv. 80).

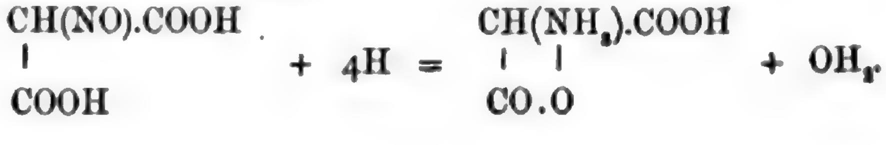
Methylsuccinic Acid Derivatives.—A number of these have been obtained by the addition of haloid acids and halogens to the three isomeric acids of the formula $C_3H_4(COOH)_2$, citra-, ita- and mesaconic acid; when submitted directly to the action of bromine, methylsuccinic or pyrotartaric acid chiefly furnishes bodies resulting from the decomposition of its bromo-derivatives (comp. Bourgoin, *Ann. Chim. Phys.* [5], xii. 419). *Mesachloropyrotartaric acid*, $C_3H_5Cl(COOH)_2$, is formed both from citraconic and mesaconic acid; it crystallizes in small shining plates, melting at 129° (264° F.); when heated with water it yields mesaconic acid. *Itachloropyrotartaric acid*, obtained by combining itaconic acid with hydrochloric acid, melts at 140°—145° (284°—293° F.), and is converted into itamalic acid (*q. v.*), $C_3H_5(OH)(COOH)_2$, when boiled with water. The corresponding bromo-acids crystallize well, and melt respectively at 148° (298°·4 F.) and 137° (278°·6 F.) (comp. Fittig and Landolt, *Ann. Chem. Pharm.*, clxxxviii. 71). Citraconic and mesaconic acids combine with bromine forming isomeric dibromopyrotartaric acids which crystallize well; the citra-acid melts at 150° (302° F.), the mesa-acid at 170° (338° F.), and the former is twice as soluble as the latter in water; both are decomposed by boiling with water, yielding bromomethacrylic acid, carbonic anhydride and water (comp. Fittig and Landolt). A third isomeride is obtained from itaconic acid, and is distinguished by its conversion into itatartaric acid (*q. v.*), $C_5H_8O_6$, by the action of bases.

Adipic Acid Derivatives.—Mono- and dibromadipic acids have been obtained by heating adipic acid with bromine, but not prepared in the pure state (Gal and Gay-Lussac). By adding bromine to a solution of hydromuconic acid in acetic acid, a dibromadipic acid, $C_6H_8Br_2O_4$, is formed, which crystallizes in nodular groups of needles, melting at about 180° (356° F.) with decomposition; and by heating hydromuconic acid with water and bromine, tri- and tetrabromadipic acids have been produced (Limpricht, *ibid.*, clxv. 264).

§ IV. AMIDO- AND HYDROXY-ACIDS DERIVED FROM THE ACIDS OF THE SUCCINIC SERIES.

So-called amidomalonic acid, asparagine, and asparaginic and glutaminic acids are the only compounds at present known which may be regarded as amido-derivatives of acids of the succinic series; it will be noticed that in many respects they closely resemble the glycines derived from the acids of the acetic series, and they may, in fact, be regarded as their carboxylated derivatives.

(1856) ***Amidomalonic*** or ***Glycinecarboxylic Acid***, $C_3H_5NO_4$, is obtained by the action of nascent hydrogen or nitrosomalonic acid, a crystalline acid obtained by the action of hydrating agents on nitrosobarbituric (violuric) acid (Baeyer, *Ann. Chem. Pharm.*, cxxxi. 291):



$$\begin{array}{l}CH(NO).COOH\\ \quad|\\ COOH\end{array} + 4H = \begin{array}{l}CH(NH_2).COOH\\ \quad|\quad\;|\\ CO.O\end{array} + OH_2.$$

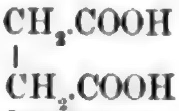
It crystallizes from an aqueous solution, concentrated by evaporation *in vacuo*, in irregular glistening prisms; it decomposes when heated either alone or in aqueous solution, yielding glycine and carbonic anhydride.

(1858) ASPARAGINE; *β-alanine-a-Carbonamide:* $C_4H_8N_2O_3$.—This substance was originally discovered in the juice expressed from asparagus shoots, but has since been shown to exist ready-formed in a large number of plants (comp. Husemann, *Die Pflanzenstoffe*). It is especially abundant in the young shoots developed on germination of leguminous seeds, being doubtless a product of the decomposition of the albuminoid bodies so largely stored up in seeds of this order; thus, according to Schulze and Umlauft (*Landwirtsch. Versuchs Stationen*, xviii. 1), no less than about one-fifth of the dry weight of young seedlings of *Lupinus luteus*, 10 to 12 centimetres in height, grown in distilled water in the dark, consists of asparagine. It has been stated that the amount produced on germination varies according as the plant is grown in the dark or exposed to light, but this does not appear to be the case (comp. Sachse, *Die Chemie der Farbstoffe, Kohlehydrate and Proteinsubstanzen*). Asparagine may be directly separated by crystallization from the juice expressed from asparagus shoots, young vetch plants, &c., its preparation being much facilitated by submitting the juice to diffusion previous to concentration. It forms colourless, hard, brittle, four-sided rhombic prisms of the formula $C_4H_8N_2O_3 + OH_2$, soluble in about 11 pts. of cold water, and 4·5 pts. of boiling water, but almost insoluble in alcohol. Asparagine exhibits all the properties of the glycines (1771) combining with acids to form salts such as the hydrochloride $C_4H_9N_2O_3Cl$, and with metallic salts like argentic nitrate; it also furnishes metallic derivatives with the less positive metals, and prevents the precipitation of cupric hydrate from cupric salts by alkalies (comp. Hofmeister, *Ann. Chem. Pharm.*, clxxxix. 6). The solution of asparagine in water or alkalies exercises lævorotatory action on polarized light, but its compounds with mineral acids are powerfully dextrorotatory (comp. Pasteur, *Ann. Chem. Phys.* [3], xxxi. 67); neither its absolute specific rotatory power nor its apparent specific rotatory power in solutions of different strengths has been determined, however. The addition of acetic acid destroys the rotatory power of asparagine (Champion and Peclet, *Compt. Rend.*, lxxxii. 819).

(1858) ASPARAGINIC OR ASPARTIC ACID: *β-alanine-a-carboxylic acid:* $C_4H_7NO_4$.—This acid is formed on boiling asparagine with acids or alkalies, and also by the action of hydrating agents on albuminoid substances both of animal and vegetable origin; it is contained in somewhat considerable quantity in beet-sugar molasses. It crystallizes in small rhombic prisms considerably less soluble than asparagine in water; it is converted into malic or hydroxysuccinic acid by nitrous acid, and into succinic acid by fermentation. Asparaginic acid combines with mineral acids in the same molecular proportions as asparagine; but it furnishes two series of metallic derivatives of the forms $C_4H_6NO_4M'$ and $C_4H_5NO_4M'_2$. Its most characteristic metallic derivative is the copper salt $2C_4H_5CuNO_4 + 9OH_2$, which may be advantageously used in preparing the pure acid: for this purpose a warm aqueous solution of the impure acid is mixed with cupric acetate and allowed to cool; it crystallizes in pale-blue aggregates of very fine needles, difficultly soluble in hot water, but moderately soluble in boiling dilute acetic acid. This salt may be dissolved in alkali without the precipitation of cupric hydrate (Hofmeister, *loc. cit.*). Asparaginic acid reduces Fehling's solution. The metallic derivatives of asparaginic acid are lævorotatory, but its compounds with acids are dextrorotatory (Pasteur); exact observations of their absolute specific rotatory power and of their apparent specific rotatory power in solutions of different strengths are wanting.

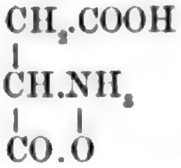
An optically inactive modification of asparaginic acid is obtained on heating the acid ammonic salt of fumaric, maleic or malic acid at 180°—200° (356—392° F.), and boiling the residue with hydrochloric acid. It closely resembles the active acid, but is somewhat more soluble in water (Dessaignes, Pasteur).

The relation of asparagine and asparaginic acid to each other and to succinic acid is most probably expressed by the following formulæ:



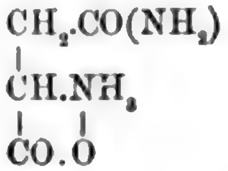
$$\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$$

Succinic acid.



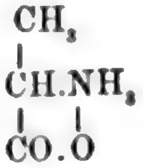
$$\begin{array}{l} CH_2.COOH \\ | \\ CH.NH_2 \\ |\quad\ | \\ CO.O \end{array}$$

Asparaginic acid.



$$\begin{array}{l} CH_2.CO(NH_2) \\ | \\ CH.NH_2 \\ |\quad\ | \\ CO.O \end{array}$$

Asparagine.



$$\begin{array}{l} CH_3 \\ | \\ CH.NH_2 \\ |\quad\ | \\ CO.O \end{array}$$

β-Alanine.

(1859) GLUTAMINIC ACID; *Tetraneglycinecarboxylic Acid:* $C_5H_9NO_4$.—This acid was first obtained by Ritthausen (*Jour. pr. Chem.*, xcix. 454; cvii. 218) by boiling gluten with dilute sulphuric acid, but it appears to be a product of the action of hydrating agents on albuminoid substances generally, both animal and vegetable, although the amount obtained from different albuminoids varies greatly (comp. Ritthausen and Kreusler, *ibid.* [2], iii. 314). It has also been separated from mangold-wurzel juice and the juice of young pumpkins which had been boiled with hydrochloric acid (Schulze and Barbieri, *Jour. Chem. Soc.*, 1877, ii. 324; Schulze and Urich, *ibid.*, 1878, i. 84); the original juice doubtless contains glutamine, the unknown amide corresponding to asparagine, which will probably in many cases be found to accompany asparagine.

Glutaminic acid crystallizes in laminæ and rhombic tetrahedra soluble in 100 pts. of water at 16° (60°·8 F.); according to Ritthausen, it melts at about 140° (275°—284° F.) with partial decomposition, but according to Hofmeister at 185° (365° F.). When slowly crystallized, its cupric salt forms well-defined deep-blue prisms of the composition $2C_5H_7CuNO_4 + 5OH_2$, soluble in boiling water; but on stirring a very concentrated hot solution with a glass rod, it is deposited in minute pale-blue prisms of the composition $C_5H_7CuNO_4 + 2OH_2$, insoluble in boiling water. On adding cupric sulphate to an alkaline solution of glutaminic acid, a precipitate forms as soon as the proportion $2C_5H_9NO_4 : CuSO_4$ is exceeded, whereas asparagine and asparaginic acid do not furnish a precipitate until double this proportion of cupric salt is added (Hofmeister). Glutaminic acid even in very dilute solution reduces Fehling's solution as easily as glucose, but the presence of leucine may interfere with the reaction although a large amount of this body has no influence on the reduction of the solution by glucose; (Hlasiwetz and Habermann, *Ann. Chem. Pharm.*, clxix. 157); this is denied by Hofmeister, *ibid.*, clxxxix. 14. Glutaminic acid forms highly characteristic well-crystallized compounds with hydrochloric and hydrobromic acid (Hlasiwetz and Habermann). It is doubtless optically active, as a solution in nitric acid is powerfully dextrorotatory, the value deduced for the apparent specific rotatory power being + 34°·7, but it has not been stated whether this is for mean yellow light or light of the refrangibility of the D line, nor what particular strength of solution gives this value.

HYDROXY-ACIDS DERIVED FROM ACIDS OF THE SUCCINIC SERIES.

(1860). The following are known:

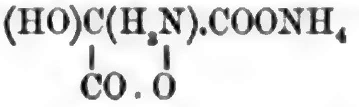
Hydroxymalonic (tartronic) acid	$CH(OH)(COOH)_2$
Dihydroxymalonic (mesoxalic) acid . . .	$C(OH)_2(COOH)_2$
Hydroxysuccinic (malic) acid	$C_2H_3(OH)(COOH)_2$
Hydroxyisosuccinic acid	$CH_3.C(OH)(COOH)_2$
Dihydroxysuccinic (tartaric) acid	$C_2H_2(OH)_2(COOH)_2$

Hydroxypropane-*a*-dicarboxylic acid	$C_3H_5(OH)(COOH)_2$
Methylhydroxysuccinic acid	$CH_3.C(OH)(COOH).CH_2.COOH$
Itamalic acid	$C_3H_5(OH)(COOH)_2$
Citramalic acid	
Itatartaric acid	$C_3H_4(OH)_2(COOH)_2$
Citratartaric acid	
Aposorbic acid	$C_3H_3(OH)_3(COOH)_2$
Dimethyltartaric acid	$[CH_3.C(OH).(COOH)]_2$
Hydroxyadipic acid	$C_4H_7(OH).(COOH)_2$
Dihydroxyadipic acid	$C_4H_6(OH)_2(COOH)_2$
Trihydroxyadipic acid	$C_4H_5(OH)_3(COOH)_2$
Saccharic acid	$C_4H_4(OH)_4(COOH)_2$
Mucic acid	
Diaterebic acid	$C_5H_9(OH)(COOH)_2$
Diaterpenylic acid	$C_6H_{11}(OH)(COOH)_2$

(1861) HYDROXYMALONIC or TARTRONIC ACID: $C_3H_4O_5 = CH(OH)(COOH)_2$.—Theoretically this acid should be formed by oxidation of glycerol, and probably it may be so produced (comp. Sadtler, *Deut. chem. Ges. Ber.*, viii. 1456), but the conditions to be observed have not yet been established. It is one of the products of the action of Fehling's copper solution on glucose (Claus); and is also formed by digesting bromomalonic acid (Petrieff) with argentic hydrate; by the action of nascent hydrogen on mesoxalic acid; and by the decomposition of dinitroxysuccinic acid (p. 945), $C_2H_2(NO_3)_2(COOH)_2$. It was first obtained by Dessaignes in 1852 by the last-mentioned method; according to Demole (*ibid.*, x. 1788), it is best prepared by gradually adding the nitroxy-acid to alcohol of sp. gr. 925 in the proportion of 20 grams of the former to 60 c.c. of the latter, the alcohol being heated in a porcelain dish on the water bath: in this manner, the destruction of the tartronic acid by the nitric acid which takes place when an aqueous solution is heated is avoided. The conversion is complete within about fifteen minutes, when the evolution of gas almost ceases and crystallization commences.

Tartronic acid crystallizes in large colourless prisms, melting at 151° (303°·87 F.) (Demole), easily soluble in water; when heated at a higher temperature, it is resolved into water, carbonic anhydride, and glycolide (1793). It furnishes a well-crystallized acid ammonic salt, and crystalline precipitates are obtained on adding baric or calcic chloride, or argentic nitrate, &c., to a neutralized solution of the acid.

(1862) DIHYDROXYMALONIC or MESOXALIC ACID: $C(OH)_2(COOH)_2 = C_3H_4O_6$—This acid may be obtained by heating alloxan and alloxanic acid with alkalies, &c., and by oxidation of amidomalonic acid (1856); according to Petrieff, it is formed on heating dibromomalonic acid with baric hydrate solution. It crystallizes in very deliquescent prisms, melting at 115° (239° F.) easily soluble in anhydrous alcohol; its aqueous solution decomposes at 70°—80° (158°—176° F.) and must be concentrated at a temperature not exceeding 50° (122° F.) when it is desired to separate the crystallized acid. Most of its salts are easily soluble and crystalline, the baric, plumbic and argentic salts alone being difficultly soluble; their composition after drying at 100° (212° F.) is represented by the formula $C_3H_2O_6M'_2$, and they cannot be deprived of the elements of water without undergoing complete decomposition (Deichsel, *Jahresb.*, 1864, 640). By adding ammonia to an alcoholic solution of the acid, a crystalline compound of the formula $C_3O_5N_2H_8$ is obtained, which reddens on exposure to the air. This has been generally regarded as an ammonic salt of the formula $CO(COONH_4)_2$, and the existence of such a compound has been held to be a proof that mesoxalic acid itself has the formula $CO(COOH)_2$; it is not improbable, however, that it is a glycine derivative of the formula



$$\begin{array}{l}(HO)C(H_2N).COONH_4\\ \quad\;\; | \quad\;\;\; | \\ \quad CO\,.\,O\end{array}$$

According to Petrieff (*Deut. chem. Ges. Ber.*, xi. 414), the true ammonic salt is obtained on neutralizing a solution of the acid with ammonic carbonate and evaporating *in vacuo*; it does not alter in the air. On treatment with acetic chloride, ethylic mesoxalate yields diacetyl derivative which is decomposed by a dilute alcoholic solution of potassic hydrate, yielding the potassic salt of diacetoxymalonic acid; this acid melts at 130° (266° F.), and its ethylic salt at 145° (293° F.) (Petrieff).

(1863) HYDROXYSUCCINIC OR MALIC ACID: $C_4H_6O_5 = COOH.CH_2.CH(OH).COOH$.—This acid, which was discovered by Scheele in 1785, is of very common occurrence in plants, both in the free state and in the form of salts, and particularly in unripe fruits, such as the apple, quince, and gooseberry; it is especially abundant in mountain-ash berries at the time when they begin to ripen, and in the stalks of the garden rhubarb. Tobacco leaves are rich in acid calcic malate.

To prepare the pure acid from the juice of plants in which it is present in considerable amount, the following method devised by Liebig may be advantageously employed. The expressed juice after being boiled and filtered is nearly neutralized with calcic hydrate, the precipitate of calcic phosphate, tartrate, &c., which forms is removed by filtration, and the clear liquid boiled for several hours in a copper pan; normal calcic malate is then deposited as a but slightly coloured sandy powder, which should be removed as it separates, the boiling being discontinued when it no longer forms. If the juice is neutralized, much of the colouring matter is carried down and a highly impure salt is obtained.

The crude calcic malate thus produced is added to a hot solution of 1 pt. nitric acid to 10 pts. water as long as it dissolves, and is thus converted into the acid salt which crystallizes from the solution on cooling in large transparent crystals, difficultly soluble in cold water. This salt is dissolved in hot water, precipitated with plumbic acetate, the precipitate well washed, suspended in water and decomposed by hydric sulphide.

Malic acid crystallizes from a highly concentrated solution in aggregates of colourless prisms; it deliquesces in moist air, and is also easily soluble in alcohol. It melts at about 100° (212° F.), and may be heated at 120° (248° F.) without loss of weight; at 140° (284° F.) it slowly loses the elements of a molecule of water and is converted into a mixture of maleic and fumaric acids, $C_4H_4O_4$; this change is more completely effected at 150° (302° F.), and if the acid be heated at about 180° (356° F.), maleic acid and anhydride distil over, a residue of fumaric acid remaining in the retort. No gas is evolved, and no carbonization takes place under these circumstances, but if it be rapidly heated to above 200° (392° F.) carbonic oxide and anhydride are evolved and much of the acid is carbonized. When very carefully oxidized by means of potassic dichromate, malic acid is converted into malonic acid (Dessaignes); when fused with potassic hydrate, it yields a mixture of acetate and oxalate; when boiled with dilute sulphuric acid (b.p. 135° C.), it is resolved into ethaldehyde, carbonic oxide and carbonic anhydride (Weith, *Deut. chem. Ges. Ber.*, x. 1744). It is converted into succinic acid by heating with a solution of hydriodic acid, and also undergoes reduction to this acid on fermentation (comp. p. 926, 8); it forms bromosuccinic acid when digested at 100° (212° F.) with an equal volume of a cold saturated solution of hydrobromic acid, but if boiled with a larger quantity of the acid it yields fumaric acid, which is also formed on boiling it with hydrochloric acid. On distillation with phosphoric pentachloride, it yields fumaric chloride, $C_2H_2(COCl)_2$.

Malates.—The most characteristic malates are the acid ammonic salt, the acid and normal calcic salts and plumbic malate. The acid ammonic salt, $C_4H_5(NH_4)O_5$, crystallizes in large rhombic prisms soluble in about 3 pts. cold water. A solution of malic acid does not yield a precipitate with lime water either in the cold or on heating, but calcic malate is thrown down on the addition of alcohol; if the solution be concentrated *in vacuo* large lustrous laminæ of a hydrated salt, $C_4H_4CaO_5 + 2OH_2$, readily soluble in water, are obtained, and on boiling down the solution of this salt, the anhydrous malate is deposited as a crystalline almost insoluble precipitate. Acid calcic malate, $(C_4H_5O_5)_2Ca + 8OH_2$, crystallizes in glistening transparent rhombic prisms, soluble in about 50 pts. cold water. Plumbic acetate added to a solution of the acid produces a white curdy precipitate which after a time becomes crystalline; it is characteristic of this salt that when heated under water it melts, but it only exhibits this property when unmixed with other salts. *Diethylic malate*, $C_4H_4O_5(C_2H_5)_2$, prepared by saturating an alcoholic solution of the acid with hydrochloric acid, is an oily liquid which decomposes on distillation into water and diethylic fumarate, $C_4H_2O_4(C_2H_5)_2$; on treatment with acetic chloride, it is converted into diethylic acetoxysuccinate, $C_2H_3(C_2H_3O_2)(COOC_2H_5)_2$; and the corresponding nitroxy-salt $C_2H_3(NO_3)(COOC_2H_5)_2$ is formed on dissolving it in a mixture of nitric and sulphuric acids.

Malic acid is usually said to be an optically active substance: thus Pasteur found the value of $[\alpha]_j$ for a solution containing about one-third of its weight of acid to be $-5°$, and Ritthausen (*Jour. pr. Chem.* [2], v. 354) gives $[\alpha]_j = -4^\circ{\cdot}74$ for a solution containing one-sixth of its weight of acid. Pasteur, however, employed for his determination a sample of acid not prepared by himself, and he states that a sample which he had himself prepared from mountain-ash berries with especial care was almost destitute of optical activity. According to Ritthausen (*Jour. pr. Chem.* [2], ii. 339), the seeds of *Lupinus luteus* contain optically inactive malic acid. The addition of boric acid increases the lævorotatory power of malic acid, but its solution in nitric acid is dextrorotatory. Acid ammonic malate in a solution containing about one-fourth its weight has the apparent specific rotatory power $[\alpha]_j = -7^\circ{\cdot}2$. Normal calcic malate is dextrorotatory, as is also its solution in hydrochloric acid; ammonic antimonyl malate in a solution containing ·068 of its weight of the salt has the high apparent specific rotatory power $[\alpha]_j = +115^\circ{\cdot}47$ (Pasteur, *Ann. Chim. Phys.* [3], xxxi. 81).

Isomeric Malic Acids.—By submitting optically active asparagine or asparaginic acid to the action of nitrous acid, a product is obtained which appears to be identical with malic acid from natural sources, but by similarly treating inactive artificially prepared asparaginic acid, an inactive acid is produced, which is somewhat less soluble than natural malic acid and melts at 133° (271°·4 F.), although it otherwise resembles the natural acid in all respects (Pasteur).

Optically inactive malic acid is also produced by digesting bromosuccinic acid with argentic hydrate, &c. (Kekulé); the properties of the product have not yet been sufficiently studied, however.

Fumaric acid, $C_2H_2(COOH)_2$, combines with the elements of a molecule of water when heated with water alone at 150° (302° F.) (Jungfleisch), or with a solution of sodic hydrate at 100° (212° F.). In the latter case, an optically inactive hydroxysuccinic acid is obtained, which appears to differ more or less from natural malic acid in all its properties, yielding, for example, only fumaric acid and water when decomposed by heating at 180°—200° (356°—392° F.) (Loydl, *Ann. Chem. Pharm.*, cxcii. 80).

By digesting tartaric acid with a solution of hydriodic acid, it is partially converted into malic acid (Dessaignes); according to Bremer (*Deut. chem. Ges. Ber.*, viii. 1594), the acid thus prepared from dextrotartaric acid is dextrorotatory, its apparent sp. rotatory power being $[\alpha]_D = 3^\circ{\cdot}15$, that of the natural acid from mountain-ash berries being $[\alpha]_D = -3^\circ{\cdot}29$. Racemic acid yields inactive malic acid. Acid ammonic dextromalate has the apparent sp. rotatory power $[\alpha]_D = 6^\circ{\cdot}3$, that of the corresponding lævomalate being $[\alpha]_D = 6^\circ{\cdot}2$. the inactive malic acid prepared from racemic acid, like this latter, is composed of two optically active acids having equal but opposite rotatory powers. On dissolving it in water, together with a single molecular proportion of cinchonine and adding a crystal of cinchonine lævomalate, Bremer (*ibid.*, xiii. 351) observed the separation of a considerable amount of cinchonine dextromalate, the acid ammonic salt from which had the apparent sp. rotatory power $[\alpha]_D = 6^\circ{\cdot}3$, the acid ammonic malate prepared from the mother liquor from these crystals was, however, lævorobatory.

(1864) HYDROXYISOSUCCINIC or ISOMALIC ACID: $C_4H_6O_5$ = (?) $CH_3.C(OH)(COOH)_2$.—This acid is prepared by carefully digesting a solution of bromisosuccinic acid (p. 935) with argentic hydrate, &c. When heated at about 160° (320° F.), it is resolved into carbonic anhydride and lactic acid, $CH_3.CH(OH).COOH$ (Schmoeger, *Jour. pr. Chem.* [2], xiv. 81).

(1865) DIHYDROXYSUCCINIC or TARTARIC ACID: $C_4H_6O_6 = COOH.CH(OH).CH(OH).COOH$.—No fewer than four distinct modifications of the acid $C_2H_2(OH)_2(COOH)_2$ are known: two of these differ merely in their optical characters, the one rotating the polarized ray to the right, the other rotating it to a precisely equal extent in the opposite direction, and are therefore termed *dextro-* and *lævotartaric acid* respectively; the third modification, *racemic* or *paratartaric acid,* although itself optically inactive may be resolved into the two active acids; the fourth modification, *mesotartaric acid,* is not only optically inactive but also incapable of being resolved into the active modifications. We shall have occasion later on to discuss more fully the constitution of these acids.

(1866) DEXTROTARTARIC ACID; *Ordinary Tartaric Acid.*—This acid is probably of universal occurrence in plants, and is usually associated with oxalic, malic and citric acids, a circumstance which indicates a close genetic relation between these acids. Dextrotartaric acid is produced, mostly together with racemic acid, by oxidation with nitric acid of the carbohydrate sorbinose (1561) and generally of the carbohydrates which furnish saccharic acid on oxidation, being doubtless a product of the oxidation of this acid. According to Debus (*Jour. Chem. Soc.*, xxv. 365), a small amount of "tartaric acid" is produced by the action of nascent hydrogen (sodium amalgam) on an alcoholic solution of ethylic oxalate: the calcic salt of the acid so obtained agrees in chemical and physical properties with calcic tartrate, but it has not been ascertained whether the optical properties of the product are those of dextrotartaric acid (*private communication*).

Dextrotartaric acid is largely used in calico-printing, to liberate chlorine from bleaching powder in the production of white or discharged patterns upon a coloured ground. It is always prepared from the crude hydric potassic tartrate deposited during the fermentation of grape juice.

The materials from which it is made may be classed as *lees*, *argol*, and *tartar*, lees being the solid matter collected from the bottoms of the fermenting vessels; argol, the thin crystalline crust deposited on the sides of these vessels; whilst tartar is manufactured from the two former by a rough process of extraction with hot water and crystallization (comp. Warington, *Jour. Chem. Soc.*, xxviii. 949). In preparing the acid, a boiling solution of the tartar is treated with powdered chalk, whereby insoluble calcic tartrate and soluble dipotassic tartrate are produced; the solution of the latter is separated from the former by filtration, and is then mixed with a soluble calcic salt, or digested with calcic sulphate, and thus the whole of the tartrate is converted into calcic salt; the percipitated calcic tartrate thus obtained, after being washed, is treated with sufficient dilute sulphuric acid to displace the whole of the calcium, and the resulting solution of tartaric acid cautiously evaporated to the crystallizing point.

Dextrotartaric acid crystallizes very readily in large, well-formed, anhydrous monoclinic prisms (comp. p. 944), soluble in about half their weight of cold water; its apparent specific rotatory power in aqueous solution at 19°—20° (66°·2—71°·6 F.) is expressed by the formula $[a]_D = 15{\cdot}06 \quad 0{\cdot}131\ C$, where C is the number of grams of acid in 100 c.c. of solution as shown by the following table (Landolt, *Deut. chem. Ges. Ber.*, vi. 1075):

C.	$[a]_D$ (Landolt).	$[a]_D$ (Arndtsen).	$[a]_D$ (calculated).
15°·38	13°·06	13°·10	13°·05
7·69	14·02	14·01	14·05
3·845	14·53	14·49	14·56
1·9225	14·87	14·73	14·81
·9612	14·92	14·85	14·93
·4806	15·03	14·92	15·00

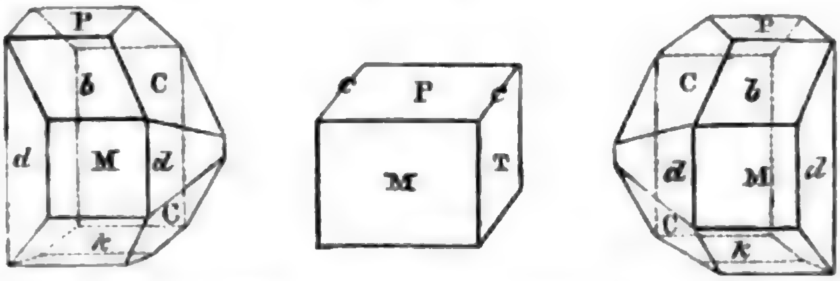
The apparent specific rotatory power varies, however, not only with the concentration, but also with the temperature, increasing with rise of temperature. Certain anomalies in its rotatory power for rays of different refrangibility will be referred to later on.

Dextrotartaric acid melts at about 170° (338° F.), and is said to be thereby converted without loss of water into the isomeric metatartaric acid; it is further stated that by prolonged heating at about 180° (356° F.) so-called *ditartaric acid,* $C_8H_{10}O_{11} = 2C_4H_6O_6 - OH_2$, is produced; then *tartrelic acid,* $C_4H_4O_5$, which is a soluble substance; and ultimately insoluble so-called *tartaric anhydride,* isomeric with the last. The existence of metatartaric acid, however, as a distinct species is very doubtful, and it is probable that the difference observed in the properties of the acid after fusion are due to the presence of a small quantity of ditartaric acid, it being apparently impossible to melt the acid without producing a certain quantity of the latter (comp. Warington, *loc. cit.*, p. 943). So-called ditartaric acid and tartaric anhydride are doubtless related to tartaric acid in the same manner that dehydroglycolic acid and glycolide are to glycolic acid.

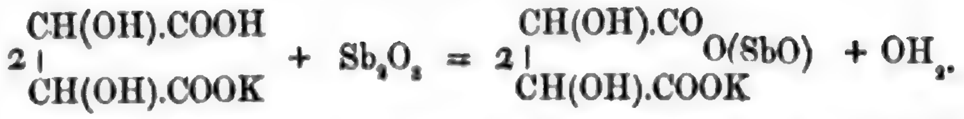
Tartaric acid is very easily oxidized, formic and carbonic acids being generally produced. When treated with hydriodic acid, it is reduced first to malic and then to succinic acid. It is readily carbonized by sulphuric acid, and is thus distinguished from malic and citric acids, which are only slowly altered. When treated with phosphoric pentachloride, it yields chloromaleic chloride, being probably first converted into dichlorosuccinic chloride, $C_2H_2Cl_2(COCl)_2$, which loses the elements of a molecule of hydrochloric acid: $C_2H_2Cl_2(COCl)_2 = C_2HCl(COCl)_2 + HCl$.

(1867) LÆVOTARTARIC ACID.—No method of directly forming this acid alone is known; it is always obtained from racemic acid (q.v.). In general chemical properties it agrees most closely with dextrotartaric acid, but undergoes fermentation less readily, in this respect resembling lævulose, which is less readily fermented than dextrose; the two acids differ, however, to a marked extent in their behaviour with other optically active substances: dextrotartaric acid, for example, forming a crystalline compound with asparagine, whereas lævotartaric acid forms with this body only an uncrystallizable syrup; in like manner, hydric ammonic dextrotartrate forms a crystalline double salt with optically active hydric ammonic malate, but hydric ammonic lævotartrate does not furnish a corresponding compound. Again, cinchonine dextrotartrate crystallizes with two molecular proportions of water, and when heated begins to decompose at about 100° (212° F.), whilst the lævotartrate crystallizes with only half a molecular proportion of water and is much more stable, being unaltered at 140° (284° F.), and quinine, brucine and strychnine dextro- and lævotartrates differ in a similar manner (Pasteur, *Ann. Chim. Phys.* [3], xxxviii. 460). According to Pasteur, dextro- and lævotartaric acids both crystallize in forms derived from a monoclinic prism, PMT: sometimes, although very rarely, the crystals are *holohedral*, but as a rule certain faces, c c (Fig. 394), truncating the edges *c*, which are fully developed on one side of the crystal, are only slightly developed on the other side; often, however, they are *hemihedral*, the faces c c being present on one side only. These faces are situated on the right side in the case of dextrotartaric acid, and on the left in the case of lævotartaric acid; the two kinds of crystals are thus non-superposable, the relation of the one form to the other being precisely that of an object to its reflected image. The crystals of both acids are pyro-electrical, and when heated and left to cool, the side on which the hemihedral faces are situated becomes positively electrified and the opposite side negatively electrified. Solutions of the two acids of the same strength deflect the plane of polarization to an exactly equal extent, but in opposite directions. In all other physical properties, however, the two acids appear to be identical.

FIG. 394.



Tartrates.—Many of the metallic tartrates crystallize in well-defined and highly characteristic forms: corresponding salts of the dextro- and lævo-acids agreeing in composition and properties, and differing only in crystalline form in the manner pointed out above for the acids themselves, being mostly hemihedral. In aqueous solution, they all deflect the plane of polarization to a greater degree than, but in the same direction as, the parent acid. The following are the most characteristic. *Hydric potassic tartrate, potassic bitartrate* or *cream of tartar*, $C_4H_5O_6K$, the chief constituent of *tartar*, forms irregular aggregates of small, hard, transparent prismatic crystals, requiring for solution about 240 pts. water at 10° (50° F.), and 15 pts. boiling water. The normal potassic salt, $C_4H_4O_6K_2$, is much more soluble, requiring only 66 pts. at 14° (57°·2 F.). The corresponding sodic salts are both easily soluble. *Potassic sodic tartrate, Rochelle* or *Seignette salt*, $C_4H_4O_6KNa + 4OH_2$, one of the most characteristic of the metallic tartrates, crystallizes in large rhombic prisms, soluble in about 15 pts. cold water. By boiling a solution of the acid potassic salt with antimonious oxide, so-called *tartar emetic* is produced, the group SbO displacing hydrogen in the group COOH, thus:



$$2\left|\begin{matrix}CH(OH).COOH\\CH(OH).COOK\end{matrix}\right. + Sb_2O_3 = 2\left|\begin{matrix}CH(OH).CO\\CH(OH).COOK\end{matrix}\right.O(SbO) + OH_2.$$

This salt crystallizes in rhombic octahedra of the composition $2C_4H_4O_6K(SbO) + OH_2$, soluble in about 14 pts. cold water; it loses the whole of its water of crystallization at 100° (212° F.), and when heated at 200° (392° F.) the anhydrous salt is deprived of the elements of a molecule of water, leaving a residue of the composition $C_4H_2O_6KSb$. Analogous compounds containing the radicles AsO, BiO, BoO, FeO, CrO and UO, are obtained by digesting solutions of hydric potassic tartrate with the oxides of arsenic, &c.

Calcic tartrate, $C_4H_4O_6Ca + 4OH_2$.—Even dilute solutions of tartaric acid yield a crystalline precipitate of this salt when treated with calcic acetate, and it is also obtained with calcic chloride in presence of alcohol; solutions of normal tartrates are also readily precipitated by calcic chloride, although if the liquors are dilute the precipitate does not appear for some minutes. Calcic tartrate is dimorphic, being frequently deposited, especially from dilute solutions, in the form of very fine needles radiating from a common centre, but after a time these are converted into isolated rhombic prisms and octahedra, which, however, are always holohedral. Solutions of calcic dextro- and lævotartrate in hydrochloric acid exert respectively a lævo- and dextrorotatory action on polarized light (Pasteur). If baric chloride be added to a dilute solution of ammonic or sodic tartrate, or if baric acetate be added to even a very dilute (1 per cent.) solution of the free acid, a precipitate of baric tartrate is produced which generally is at first bulky and flocculent, but in a few hours this precipitate disappears and the sides of the vessel become coated with clean globular masses (Warington). So-called basic tartrates are obtained by displacing the hydrogen of the OH groups as well as that in the COOH groups, by the less positive metals. Thus, if plumbic tartrate, $C_4H_4O_6Pb$, be dissolved in ammonia solution, and the liquid boiled, a precipitate of the composition $C_2H_2(O_2Pb).(COO)_2Pb$ is obtained. Similarly, cupric hydrate dissolves in solutions of normal tartrates of alkali metals, furnishing a solution not precipitable by alkalies, and in like manner the precipitation of aluminium, iron, tin, &c., by alkalies is prevented by the presence of an alkali metal tartrate, no doubt owing to the formation of mixed basic tartrates. Fehling's solution used in the estimation of glucose, &c., is a solution of a basic salt of this kind in excess of alkali.

Ethylic tartrate, $C_4H_4O_6(C_2H_5)_2$, prepared by saturating a solution of tartaric acid in ethylic alcohol with hydrochloric acid, is a colourless liquid which decomposes on distillation. By the action of an excess of acetic chloride, it is converted into *ethylic diacetoxysuccinate*, $C_2H_2(C_2H_3O_2)_2(COOC_2H_5)_2$, a crystalline substance which melts at 67° (152°·6 F.), and distils with only slight decomposition (Perkin, *Jour. Chem. Soc.*, xx. 147). By the action even of an excess of benzoic chloride on ethylic tartrate, only the hydrogen of one of the OH groups becomes displaced by benzoyl, although on treating the monobenzoyl derivative thus obtained with acetic chloride, acetyl is readily introduced in place of the hydrogen of the second OH group (Perkin).

If tartaric acid be digested for several hours with about three times its weight of acetic chloride, it is gradually converted into *diacetotartaric* or *diacetoxysuccinic anhydride*, $C_2H_2(C_2H_3O_2)_2.C_2O_3$, a crystalline solid melting at 126° (258°·8 F.); it combines with water, forming the corresponding acid, dimetallic salts of which may be obtained by neutralization with metallic carbonates, &c. (Perkin).

If tartaric acid be dissolved in 4–5 pts. of the strongest nitric acid, and an equal volume of concentrated sulphuric acid be then added to the solution with constant stirring, a pasty mass of *dinitroxysuccinic acid*, $C_2H_2NO_3)_2(COOH)_2$, is produced; this may be purified by spreading on porous tiles, crystallization from water at 0° (32° F.), and recrystallization from ether (comp. Demole, *Deut. chem. Ges. Ber.*, x. 1789). It is an extremely unstable body, decomposing into tartronic acid, &c., at a few degrees above 0° (32° F.) even in aqueous solution.

(1868) RACEMIC ACID.—This acid was discovered in 1822 by Kestner, a manufacturer of tartaric acid at Thann in the Vosges, who obtained it in large quantity from tartars produced in the vintages of 1822—1824. It was not again observed, however, for many years, and on inquiry Pasteur ascertained that this was chiefly owing to the fact that the manufacturers of tartaric acid had ceased to make use of the crude tartars and were employing tartar partially purified by crystallization; crude tartars from various districts were all found to contain more or less racemate, but being more soluble than the tartrate this chiefly remained in the mother-liquors.

Racemic acid may be formed by the direct union of dextro- and lævotartaric acid: on mixing cold saturated solutions containing equal weights of the two acids, heat is developed, and racemic acid separates out as the solution cools.

According to Pasteur, the acid which Perkin and Duppa and Kekulé obtained by digesting argentic dibromosuccinate with water, or calcic dibromosuccinate with lime water, is a mixture of racemic and mesotartaric acids; Jungfleisch (*Compt. Rend.*, lxxvi. 286) has shown that racemic acid can be obtained in this way from succinic acid prepared from ethylene, and consequently, since racemic acid may be resolved into dextro- and lævotartaric acid, that it is possible to produce optically active substances by entirely artificial means. Racemic acid is also formed (*a*) by digesting a mixture of oxaldehyde (glyoxal, 1667) and hydrocyanic acid with hydrochloric acid (Strecker). (*b*) By oxidation of a number of carbohydrates and of saccharic and mucic acids: in most cases, dextrotartaric acid is also produced, the following, according to Hornemann (*Jour. pr. Chem.*, lxxxix. 283), being the relative amounts of the two acids obtained:

	Dextrotartaric acid.		Racemic acid.
Dextroglucose	100	...	—
Lævoglucose	—	...	100
Cane sugar	59·7	...	40·3
Milk sugar	55·4	...	44·6
Starch	100	...	—
Gum	63	...	37
Saccharic acid	72·6	...	27·4
Mucic acid	?	...	100

(*c*) By heating either dextro- or lævotartrate of cinchonine for five or six hours at 170° (338° F.); mesotartaric acid is also produced simultaneously, the amount increasing as the heating is prolonged (Pasteur). Other tartrates, such as ethylic tartrate and quinine tartrate, are also converted into racemates on heating (Pasteur). (*d*) By heating mesotartaric acid, or by boiling it with hydrochloric acid (Dessaignes). (*e*) Together with mesotartaric acid and decomposition products by heating dextrotartaric acid with about one-tenth of its weight of water for about 30 hours at 175° (347° F.); if the heating be continued long enough, the whole of the dextrotartaric acid disappears, racemic and mesotartaric acids being formed in proportions which vary with the degree of heat and quantity of water added; and by heating mesotartaric acid alone with water in a similar manner, it is also transformed into racemic acid, but it cannot be completely converted by one treatment. To separate the racemic acid, the product of the action of heat is dissolved in boiling water, the solution filtered and evaporated; if the concentration be not carried too far, the crystals which separate on cooling consist entirely of racemic acid: 650 grams dextrotartaric acid heated with 100 grams of water in a metal digester yield in a single operation more than 100 grams racemic acid (Jungfleisch, *Bull. Soc. Chem.* [2], xviii. 201). (*f*) By the decomposition of desoxalic acid (1882).

Racemic acid crystallizes in triclinic prisms of the composition $C_4H_6O_6 + OH_2$, which effloresce on exposure to the air and become completely anhydrous at 100° (212° F.); the anhydrous acid melts at about 200° (392° F.). Racemic acid is less soluble in water than tartaric acid, the crystallized acid requiring 5—7 pts. water at 15° (59° F.); its solution is optically inactive. It is also distinguished from tartaric acid by the behaviour of its calcic salt, which, although of the same composition, is less soluble than calcic tartrate, being precipitated on adding calcic chloride or sulphate to a solution of the acid; calcic racemate also is insoluble in acetic acid, and on adding ammonia to its solution in hydrochloric acid, a crystalline precipitate forms within a few seconds, whereas with calcic tartrate the precipitation does not take place for several hours.

The racemates all crystallize in holohedral forms, and are optically inactive. According to Pasteur, the property of uniting to form a racemate does not obtain for all metallic dextro- and lævotartrates; thus if a solution of racemic acid be divided into two equal portions and the one half neutralized with sodic carbonate, the other with potassic carbonate or ammonia, and the two solutions mixed, the liquid being of such a degree of concentration that it only deposits crystals after some hours, the crystals which form consist not of sodic potassic or sodic ammonic racemate, but in part of the corresponding dextro- and in part of the corresponding lævotartrate. It was in this way, in fact, that Pasteur originally ascertained the nature of racemic acid, and succeeded in resolving it into dextrotartaric acid and the then unknown lævotartaric acid. It would appear, however, that under certain conditions a solution prepared in the manner described with the aid of sodic carbonate and ammonia also deposits holohedral monoclinic crystals of sodic ammonic racemate (comp. Städel, *Deut. chem. Ges. Ber.*, xi. 1852).

Fig. 395.

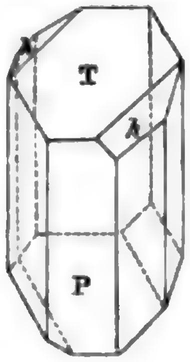


Fig. 396.

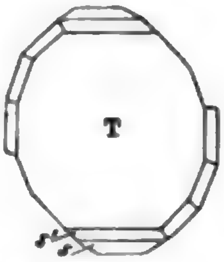
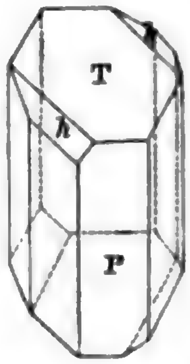


Fig. 397.



The crystalline form of the two sodic ammonic tartrates is represented by Figs. 395, 396, although in reality they are somewhat more complicated as shown by Fig. 397, which is a projection of the extremity of a crystal of dextrotartrate. The crystals being so placed that the face P is in front of the observer and the face T horizontal, it will be seen that there is a hemihedral face *h* on the right hand in the case of the dextrotartrate, and on the left hand in the case of the lævotartrate; the face P is readily recognised in consequence of the presence of the small faces *s*, *s*, Fig. 396, which truncate the edge formed by the intersection of the faces P and T.

(1869) MESOTARTARIC ACID.—This modification is formed together with racemic and dextrotartaric acid by oxidation of sorbinose (1561), and together with racemic acid by digesting dibromosuccinic acid with water and a metallic hydrate; it may also be produced by heating cinchonine dextrotartrate or racemate for several hours at 170° (348° F.), by prolonged boiling of dextrotartaric or racemic acid with hydrochloric acid, and by heating either of these acids with water. It is best prepared by heating dextrotartaric acid with about one-tenth its weight of water for two days at 165° (329° F.) (comp. Jungfleisch, *loc. cit.*).

Mesotartaric acid is very soluble in water and usually crystallizes in rectangular plates of the composition $C_4H_6O_6+OH_2$, which readily part with their water at 100° (212° F.); if the anhydrous acid be dissolved in water and the solution be allowed to crystallize, large anhydrous holohedral crystals resembling those of dextrotartaric acid are deposited. It melts at 140° (284° F.). Mesotartaric acid is optically inactive and cannot be resolved into the active modifications, but it may be converted into racemic acid by heating with water at 175° (347° F.) (Jungfleisch). Calcic and hydric potassic mesotartrate are more soluble than the corresponding tartrates.

(1870) HYDROXYPROPANE-α-DICARBOXYLIC ACIDS.—Two such acids are known, the one formed by heating so-called dichlorhydrin $(CH_2Cl)_2CH.OH$ (p. 541) with potassic cyanide, &c.; the other by the action of nitrous acid on glutaminic acid. The former is a crystalline body, melting at 135° (275° F.); judging from the manner in which it is prepared it should have the formula $CH_2(COOH).CH(OH).CH_2(COOH)$ (Maxwell Simpson, *Proc. Roy. Soc.*, xiii. 44). The latter has been termed *glutanic* acid; it is very soluble in water and crystallizes with difficulty; it melts at about 73° (163°·4 F.) (comp. Markownikoff, *Ann. Chem. Pharm.*, clxxxii. 347). Being isomeric with the acid from dichlorhydrin, it should have the formula $CH_2(COOH).CH_2.CH(OH).COOH$, but this is by no means established.

(1871) METHYLHYDROXYSUCCINIC or HYDROXYPYROTARTARIC ACIDS.—By heating ethylic acetoacetate at 100° (212° F.) with half its weight of anhydrous hydrocyanic acid and digesting the product with hydrochloric acid, it is converted into an hydroxy-acid of the formula $CH_3.C(OH)(COOH).CH_2.COOH$, which crystallizes in groups of deliquescent needles. When distilled, this acid is partly resolved into water and citraconic anhydride, and partly into isopropylic alcohol and carbonic anhydride. (Demarçay, *Compt. Rend.*, lxxxii. 1337; Norris, *Jour. Chem. Soc. Trans.* 1880, 6.)

By combining itaconic acid, $C_3H_4(COOH)_2$, with hydrochloric or hydrobromic acid, and boiling the resulting chloro- or bromo-acid with water for 6–8 hours, so-called *itamalic* acid, $C_3H_5(OH)(COOH)_2$, is produced; this crystallizes in long needles, melting at 64° (147°·2 F.) (Swarts; comp. Fittig and Landolt, *Ann. Chem. Pharm.*, clxxxviii. 71). Citra- and mesaconic acids do not appear to furnish hydroxy-acids when treated like itaconic acid, as above described (comp. Fittig and Landolt, *loc. cit.*), but according to Carius, *citramalic acid*, isomeric with itamalic acid, may be obtained by combining citraconic acid with hypochlorous acid, and displacing the chlorine in the resulting chlorocitramalic acid by hydrogen. By combining citraconic and itaconic acids with hypochlorous acid, and boiling the products with water, isomeric dihydroxy-acids, homologous with tartaric acid, and therefore termed *citra-* and *ita-tartaric acid*, are said to be formed (Carius, *ibid.*, cxxix. 159; Wilm, clxi. 28), but these acids have been very insufficiently investigated.

(1872) APOSORBIC ACID, $C_5H_8O_7 = C_3H_3(OH)_3(COOH)_2$, is one of the products of the oxidation of sorbinose (1561) by nitric acid; it usually crystallizes in confused laminæ, but sometimes forms thin acute rhombohedra, soluble in 163 pts. water at 15° (59° F.) (Dessaignes, *Ann. Chem. Pharm.*, *Supp.*, ii. 242).

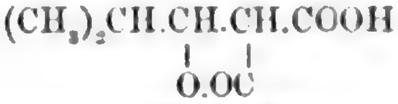
(1873) HYDROXYADIPIC ACIDS.—Mon-, di-, and trihydroxyadipic acids have been prepared from the corresponding bromo-acids (p. 935), but comparatively little is known of their properties.

(1874) **Dimethyltartaric Acid**, $[C(CH_3)(OH)(COOH)]_2$, is obtained in small quantity on dissolving zinc in a dilute alcoholic solution of acetoformic acid (1820); its hydric potassic salt crystallizes in small glistening plates, very difficultly soluble in cold water. The baric and calcic salts also crystallize well, and are almost insoluble in cold water (Böttinger, *ibid.*, clxxxviii. 315).

(1875) **Diaterebic Acid**: $C_7H_{12}O_5 = C_3H_7\beta.CH(OH).CH(COOH)_2$.—When oxidized with nitric acid (sp. gr. 1·18—1·16), both French and American turpentine oil yield a crystalline acid of the composition $C_7H_{10}O_4$, which is termed *terebic acid*. This acid is monobasic, but on treatment with alkaline hydrates it furnishes salts derived from an acid of the composition $C_7H_{12}O_5$; these *diaterebinates*, however, are uncrystallizable, and the acid which they furnish when treated with mineral acids cannot be isolated but breaks up into terebic acid and water. Terebic acid separates from alcohol in large, transparent, monoclinic crystals, slightly soluble in cold, more readily in hot water; it melts at 174° (345°·2 F.), and on distillation is completely resolved into carbonic anhydride and pyroterebic acid, $C_6H_{10}O_2$. Pyroterebic acid yields isobutyric and acetic acid on fusion with potassic hydrate (C. Williams), and is converted into isobutylacetic acid by heating with hydriodic acid; the most probable formulæ of diaterebic, terebic and pyroterebic acid are therefore as follows (Fittig and Mielck, *Ann. Chem. Pharm.*, clxxx. 45; comp. Erlenmeyer, *Deut. chem. Ges. Ber.*, xiii. 305):

$$(CH_3)_2CH.CH(OH).CH(COOH)_2$$

Diaterebic acid.



$$(CH_3)_2\underset{}{CH}.CH.CH.COOH \quad \text{with } O.OC$$

Terebic acid.

$$(CH_3)_2CH.CH{=}CH.COOH.$$

Pyroterebic acid.

(1876) **Diaterpenylic Acid**: $C_8H_{14}O_5$.—This acid is homologous with diaterebic acid, and like it cannot be obtained in the free state on account of its instability and tendency to break up into water and the dehydro-acid, *terpenylic acid*, $C_8H_{12}O_4$, homologous with terebic acid. Terpenylic acid is produced together with a small amount of terebic acid on oxidizing American or French turpentine oil, lemon oil, or so-called terpin—the crystalline glycol of the composition $C_{10}H_{18}(OH)_2$ obtained by the combination of the elements of 2 mols. water with 1 mol. of a terpene—an amount equal to about 6—7 per cent. of the weight of the terpene employed being obtained. It forms large, well-defined, triclinic prisms of the composition $C_8H_{12}O_4 + OH_2$, moderately soluble even in cold water; the pure anhydrous acid melts at 90° (194° F.). It is comparatively easily oxidized, and yields only acetic and carbonic acids. When distilled, it is resolved into carbonic anhydride and teracrylic acid, $C_7H_{12}O_2$, homologous with pyroterebic acid; but a considerable portion is converted into oily non-acid substances. The salts of terpenylic acid have the formula $C_8H_{11}M'O_4$, the most characteristic being the cupric salt; crystalline baric diaterpenylate may be obtained by adding an excess of baric hydrate to a solution of terpenylic acid, removing the excess of baric hydrate by means of carbonic acid, and concentrating the solution *in vacuo*: it is more soluble in cold than in hot water (Fittig and Hempel, *Ann. Chem. Pharm.*, clxxx. 71; Krafft, *Deut. chem. Ges. Ber.*, x. 521, 1659).

(1877) **Saccharic Acid**; *Tetrahydroxyltetranedicarboxylic Acid*: $C_6H_{10}O_8 = C_4H_4(OH)_4(COOH)_2$.—This acid is a product of the oxidation by means of nitric acid of mannitol, of the glucoses which furnish mannitol when hydrogenized, of cane sugar and of starch; it is also formed together with the isomeric mucic acid when milk sugar is similarly treated.

It is best prepared by heating 1 pt. cane sugar with 3 pts. nitric acid sp. gr. 1·3) until reaction commences; after the first brisk action is over, the mixture is maintained at 50° (122° F.) for some time, and it is then diluted with about half its bulk of water, neutralized with potassic carbonate, supersaturated with acetic acid, and allowed to stand, when slightly soluble hydric potassic saccharate crystallizes out in the form of brownish crusts. It may be purified by recrystallization with the aid of animal charcoal. To prepare the free acid, this salt is converted into the normal potassic salt, which is precipitated with cadmic sulphate, and the cadmic salt decomposed with hydric sulphide.

Saccharic acid has hitherto only been obtained as an amorphous deliquescent substance, easily soluble in alcohol; it begins to decompose when heated slightly above 100° (212° F.). It is said to exert a dextrorotatory action on polarized light. It yields dextrotartaric acid when oxidized with nitric acid; when heated with hydriodic acid it yields adipic acid (De la Motte, *Deut. chem. Ges. Ber.*, xii. 1571); on treatment with acetic chloride, it yields a crystalline compound of the formula $C_{10}H_{10}O_8$, which is probably a diacetylated anhydro-derivative (Baltzer).

The acid saccharates of the alkali metals are difficultly soluble like the acid tartrates, but the normal saccharates of alkali metals are very soluble; the saccharates of other metals are difficultly soluble or insoluble. *Ethylic saccharate*, $C_6H_8O_8(C_2H_5)_2$, is crystalline, but difficult to obtain in a pure state; it forms a crystalline compound with calcic chloride, $2C_6H_8O_8(C_2H_5)_2 + CaCl_2$, which is converted into the tetracetyl derivative $C_4H_4(C_2H_3O_2)_4(CO_2C_2H_5)_2$ by treatment with acetic chloride: this compound crystallizes from alcohol in flakes, melting at 61° (141°·8 F.) (Baltzer).

(1878) MUCIC ACID, $C_6H_{10}O_8 = C_4H_4(OH)_4(COOH)_2$, isomeric with saccharic acid is formed by oxidation of dulcitol, lactose, milk sugar, gum arabic and vegetable mucus. It is easily prepared by heating milk sugar with nitric acid until a brisk reaction sets in, and when the action has subsided again heating for a short time; as the liquid cools, it separates as a sandy crystalline powder (comp. Limpricht, *Ann. Chem. Pharm.*, clxv. 253).

Mucic acid crystallizes in plates, almost insoluble in cold water and alcohol, and it even requires about 66 pts. boiling water to dissolve it. When heated, it melts and decomposes, yielding formic acid and small quantities of pyromucic and isopyromucic acids, $C_5H_4O_3$, together with products of more complete decomposition. It yields racemic acid on oxidation with nitric acid; when heated at 100° (212° F.) with a solution of hydrobromic acid saturated at 0° (32° F.), it is converted into dehydromucic acid, $C_4H_2O(COOH)_2$ (Heinzelman, *Ann. Chem. Pharm.*, cxciii. 184). When boiled for a length of time with water, it is said to be converted into the isomeric *paramucic acid*, which is distinguished from it by its greater solubility in water; this acid, however, very readily undergoes reconversion into mucic acid—*e.g.*, on merely cooling a boiling saturated aqueous solution.

Mucic and saccharic acid are both converted by the action of phosphoric pentachloride into so-called chloromuconic chloride, $C_4H_2Cl_2(COCl)_2$, which yields chloromuconic acid, $C_4H_2Cl_2(COOH)_2$, when decomposed by water (comp. *Deut. chem. Ges. Ber.*, xii. 1271, 1571):

$$C_4H_4(OH)_4(COOH)_2 + 6PCl_5 = C_4H_4Cl_4(COCl)_2 + 6POCl_3 + 6HCl;$$
$$C_4H_4Cl_4(COCl)_2 = C_4H_2Cl_2(COCl)_2 + 2HCl.$$

The mucates are mostly insoluble, even the normal salts of the alkali metals being sparingly soluble; the acid potassic salt is somewhat more soluble than the normal salt. Ethylic mucate crystallizes in four-sided prisms, melting at 158° (316°·4 F.) (comp. Limpricht); by treatment with acetic chloride, it is converted into the tetracetyl-derivative, $C_4H_4(C_2H_3O_2)_4(CO_2C_2H_5)_2$, which crystallizes from hot alcohol in needles, melting at 177° (350°·6 F.).

Inasmuch as they are formed from mannitol and dulcitol respectively, both saccharic and mucic acid must in all probability be represented by the formula:

$$COOH.CH(OH).CH(OH).CH(OH).CH(OH).COOH;$$

we do not know, however, that both have the same molecular weight.

§ V. Tribasic Acids derived from the Paraffins.

(1879) Tricarballylic Acid; *Propanetricarboxylic Acid:* $C_6H_8O_6 =$ $COOH.CH_2.CH(COOH).CH_2.COOH$.—This acid was originally obtained by digesting *a*-tribromopropane (so-called tribromhydrin), $CH_2Br.CHBr.CH_2Br$, with an alcoholic solution of potassic cyanide, and boiling the resulting cyanide with water and an alkali (Maxwell-Simpson). It is also formed by the action of nascent hydrogen on aconitic acid, $C_6H_6O_6$ (Wichelhaus); by boiling ethylic *a*-chlorocrotonate with an alcoholic solution of potassic cyanide (Claus, *Ann. Chem. Pharm.*, cxci. 63), and by decomposing ethylic acetotricarballylate (p. 913—the product of the action of ethylic chloracetate on the sodium derivative of ethylic acetosuccinate) with a concentrated solution of potassic hydrate.

Tricarballylic acid crystallizes in transparent rhombic prisms, easily soluble in water; it melts at about 158° (316°·4 F.), but sublimes below this temperature. It does not appear to furnish characteristic or well-crystallized salts.

(1880) Citric Acid; *Hydroxytricarballylic* or *Hydroxypropanetricarboxylic Acid:* $C_6H_8O_7 = C_3H_4(OH)(COOH)_3$.—This acid occurs in the free state in many fruits, such as lemons, oranges, gooseberries and mulberries; and occasionally is met with as acid potassic or calcic salt, occurring in these forms in potatoes, for example.

It is now prepared almost entirely from lemon-juice expressed from windfalls and imperfect fruit, nearly the whole of the juice used in this country being imported from Sicily and South Italy. The amount of acid in the juice varies according to the season at which it is expressed, Sicilian juice expressed in November containing about 9 oz. per gallon, while that obtained at the end of the following April contains only about 6 oz. per gallon (Warington, *Jour. Chem. Soc.*, xxviii. 927). The hot juice is neutralized partially with calcic carbonate and partially with calcic hydrate; the precipitated calcic citrate is collected, washed, and treated with the equivalent amount of dilute sulphuric acid; and the solution of citric acid thus obtained, after being separated from the calcic sulphate, is evaporated to the crystallizing point.

Citric acid crystallizes in large transparent rhombic prisms of the composition $C_6H_8O_7 + OH_2$, very soluble in water and alcohol; the crystals may be entirely deprived of their water, without undergoing fusion, if heated for some time at 50°—60° (122°—140° F.) and afterwards at 100° (212° F.). At higher temperatures, the acid is deprived of the elements of a molecule of water, and converted into aconitic acid (q.v.), $C_3H_3(COOH)_3$, and a similar change takes place on heating it with a concentrated solution of hydrochloric or hydrobromic acid. Oxidizing agents readily completely decompose citric acid; it is also completely decomposed by sulphuric acid, but does not blacken so easily as tartaric acid when heated with this acid. It is also extremely sensitive to the action of certain organized ferments. Nascent hydrogen is without action upon it (Claus). By treating solutions of alkaline citrates with chlorine or bromine, haloid derivatives of acetone and chloroform or bromoform are produced.

Citric acid has a pure and agreeable acid taste, but it cannot be very exactly determined by neutralization with standard alkali, as it gives no sharp reaction either with litmus, cochineal or logwood (Warington). The citrates of the alkali metals are very soluble; those of other metals are mostly difficultly soluble.

Calcic citrate, $(C_6H_5O_7)_2Ca_3 + 4OH_2$, the most characteristic citrate, is more soluble in cold than in hot water, so that a cold saturated solution becomes turbid on being boiled; it is distinguished by this property from calcic tartrate, and also by its insolubility in alkalies. Citric acid, like tartaric and many other hydroxy-acids, prevents the precipitation of ferric hydrate from solutions of ferric salts by alkalies, doubtless because a ferric compound is formed by the displacement of the hydrogen of the OH group associated with the hydrocarbon radicle. Ethereal salts of citric acid are formed by saturating solutions of citric acid in the carbinols with hydrochloric acid. *Trimethylic citrate* crystallizes in well-formed triclinic prisms, melting at 79° (174°·2 F.); it is converted into the compound $C_3H_4(C_2H_3O_2)(CO_2CH_3)_3$ on treatment with acetic chloride (Hunäus, *Deut. chem. Ges. Ber.*, ix. 1749). Citric acid is converted into the highly unstable crystalline nitroxy-derivative $C_3H_4(NO_3)(COOH)_3$ by treatment with a mixture of concentrated nitric and sulphuric acid (Champion and Peclet).

(1882) DIHYDROXYPROPANETRICARBOXYLIC ACID; *Dihydroxytricarballylic* or *Hydroxycitric Acid:* $C_6H_8O_8 = C_3H_3(OH)_2(COOH)_3$, is formed by combining aconitic acid with hypochlorous acid and heating the product with water; it does not crystallize (Parvolleck, *Ann. Chem. Pharm.*, clxxviii. 510).

(1883) DESOXALIC ACID: $C_6H_8O_9$.—By acting on ethylic oxalate (containing alcohol) with sodium amalgam, Löwig in 1860 obtained the ethylic salt of a tribasic acid to which he gave the formula $C_5H_6O_8$. Brunner subsequently stated (*Deut. chem. Ges. Ber.*, iii. 974; xii. 542) that the primary product is the ethylic salt of an acid of the formula $C_6H_8O_9$, the acid corresponding to which cannot be isolated, as it decomposes on evaporation of its aqueous solution into racemic and dihydroxy-acetic (glyoxalic) acids. Klein (*Jour. pr. Chem.* [2], xx. 146), however, has recently confirmed Löwig's statements, and further investigated the acid. *Triethylic desoxalate*, $C_5H_3O_8(C_2H_5)_3$, crystallizes in triclinic prisms melting at 85° (185° F.); it yields a diacetyl-derivative on treatment with acetic anhydride. Desoxalic acid is crystalline, but very hygroscopic; on heating its aqueous solution above 45° (113° F.) it is decomposed into carbonic anhydride and racemic acid, $C_5H_6O_8 = CO_2 + C_4H_6O_6$. The racemic acid thus obtained agrees with ordinary racemic acid in all its reactions, but appears to differ from the latter in its crystallographic form.

The decomposition of desoxalic acid in this manner, and the fact that it is a tribasic penthydric acid, necessitate the conclusion that it has the following formula:

$$\begin{array}{l} C(OH)(COOH)_2 \\ \vert \\ CH(OH).(COOH), \end{array}$$

§ VI. ACIDS OF THE $C_nH_{2n-1}COOH$ OR ACRYLIC SERIES.

The acids of this series bear precisely the same kind of relation to the acids of the acetic series that the olefines bear to the paraffins, and the alcohols of the allylic series do to the alcohols of the ethylic series.

(1883) The following are at present known:

$C_3H_4O_2$	Acrylic acid	$CH_2{=}CH.COOH$
$C_4H_6O_2$	Crotonic or α-methacrylic acid . .	$CH_3.CH{=}CH.COOH$
	Isocrotonic acid	(?)$CH_3.CH{=}CH.COOH$
	β-Methacrylic acid	$CH_2{=}C(CH_3).COOH$
$C_5H_8O_2$	α²-Dimethacrylic acid	$(CH_3)_2C{=}CH.COOH$
	αβ-Dimethacrylic or methylcrotonic acid	$CH_3.HC{=}C(CH_3).COOH$
	Angelic acid	(?)$CH_3.HC{=}C(CH_3).COOH$
	Allylacetic acid	$CH_2{=}CH.CH_2.CH_2.COOH$

$C_6H_{10}O_2$	Hydrosorbic acid or (?) α-propylacrylic	$C_3H_9CH.COOH$
	α-Isopropylacrylic or pyroterebic acid	$C_3H_7\beta.HC{=}CH.COOH$
	α-Methyl-β-ethylacrylic or ethylcrotonic acid	C_5H_9
	Teracrylic acid	$C_6H_{17}.COOH$
	Damaluric acid	(?)$C_6H_{11}.COOH$
	Moringic acid	(?)$C_{14}H_{27}.COOH$
	Cimicic acid	$C_{14}H_{27}.COOH$
	Hypogæic acid	$C_{15}H_{29}.COOH$
	Oleic acid	$C_{17}H_{33}.COOH$
	Doeglic acid	$C_{18}H_{35}.COOH$
	Brassic or erucic acid	$C_{21}H_{41}.COOH$

(1884) *Methods of formation.*—1. By oxidation of the corresponding aldehydes :

$$\underset{\text{Acrylic aldehyde.}}{C_2H_3.COH} + (O + OH_2) = \underset{\text{Acrylic acid.}}{C_2H_3.COOH} + OH_2.$$

As the acids themselves very readily undergo oxidation, it is necessary to employ very mild oxidizing agents, such as argentic hydrate, for this purpose.

2. By the removal of the elements of a molecule of water from certain acids of the lactic series (comp. 1, 1784) by mere dry distillation :

$$\underset{\text{α-Hydroxypropionic acid.}}{CH_2(OH).CH_2.COOH} = \underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + OH_2$$

3. By the removal of the elements of a molecule of haloid acid from monohaloid derivatives of the acids of the acetic series, either by mere heating or by means of an alcoholic solution of potassic hydrate.

4. By the removal of a molecule of halogen from certain dihaloid derivatives of acids of the acetic series by means of nascent hydrogen :

$$\underset{\text{αβ-Dibromopropionic acid.}}{CH_2Br.CHBr.COOH} + 2H = \underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + 2HBr.$$

5. A number of the acids of the series occur naturally as ethereal salts in vegetable oils.

(1885) *Properties.*—In addition to the ordinary reactions characteristic of all compounds containing the group COOH, the acids of the acrylic series are capable, like the hydrocarbons of the olefine series from which they are derived, of uniting with the haloid acids and halogens to form haloid derivatives of the corresponding acids of the acetic series, thus :

$$\underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + HI = \underset{\text{α-Iodopropionic acid.}}{CH_2I.CH_2.COOH}.$$

The isomeric acids, however, manifest considerable differences in this respect, combining with haloid acids, &c., with very unequal degrees of facility.

2. Some few of the acids of the series may be directly converted into the corresponding acids of the acetic series by the action of nascent hydrogen:

$$\underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + 2H = \underset{\text{Propionic acid.}}{CH_3.CH_2.COOH}.$$

3. Most characteristic of the acids of the acrylic series, however, is their behaviour on fusion with potassic hydrate, whereby they are always decomposed in the manner illustrated by the following examples:

$$\underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + 2KOH = \underset{\text{Potassic formate.}}{H.COOK} + \underset{\text{Potassic acetate.}}{CH_3.COOH} +$$

$$\underset{\text{Crotonic acid.}}{H_2.CH_3.CH{=}CH.COOH} + 2KOH = \underset{\text{Potassic acetate.}}{2CH_3.COOK} + H_2.$$

In other words, the chain of carbon atoms is severed at the point of double union and the place of the C_nH_{2n} radicle which is thus split off is supplied by two atoms of hydrogen, a molecule of an acid of the acetic series being thereby produced; the C_nH_{2n} group which is separated becomes oxidized and furnishes a second molecule of an acid of the acetic series if of the form $H_2C{=}$ or $C_nH_{2n+1}HC{=}$.* A precisely similar disruption of the chain of carbon atoms results from the action of oxidizing agents such as nitric and chromic acid, but when they are employed, the group from which the C_nH_{2n} radicle is separated is oxidized instead of being hydrogenized.

4. Many of the acids of the acrylic series readily undergo isomeric change and polymerization.

(1886) ACRYLIC ACID; *Ethylenecarboxylic* or *Methenylacetic Acid*: $C_3H_4O_2{=}CH_2{=}CH.COOH$.—This acid may be formed—1. by oxidation of acraldehyde (acrolein, 1647); 2. by distilling *a*-hydroxypropionic (hydracrylic) acid; 3. by heating *a*-iodopropionic acid, $CH_2I.CH_2.COOH$, with an alcoholic solution of potassic hydrate (Erlenmeyer and V. Schneider), or by distilling it from finely pulverized plumbic oxide (Wislicenus); 4. by the action of nascent hydrogen from zinc and sulphuric acid on $a\beta$-dibromopropionic acid, $CH_2Br.CHBr.COOH$ (Caspary and Tollens), or by boiling this acid with an aqueous solution of potassic iodide (V. Zotta, *Ann. Chem. Pharm.*, cxcii. 102). It is best prepared either by oxidizing an aqueous solution of acraldehyde with freshly precipitated argentic hydrate, the reaction being allowed to take place in the cold; or by distilling α-iodopropionic acid with plumbic oxide. The anhydrous acid is obtained by heating the anhydrous lead salt mixed with an equal weight of sand at 170° (338° F.) in a current of hydric sulphide, the product being purified by fractional distillation.

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* If of the form $(C_nH_{2n+1})_2C{=}$, it would probably furnish at least two molecules of acid, but no acids of the acrylic series containing radicles of this form have as yet been examined.

At ordinary temperatures acrylic acid is a mobile liquid having a pungent and highly characteristic odour; according to Linnemann, it solidifies when cooled below 7° (44°·6 F.) and boils at 140° (284° F.). It is miscible in all proportions with water, and readily volatilizes in a current of water vapour. Like acetic acid, it furnishes a red colour with ferric chloride in neutral solutions, and also yields a strongly alkaline solution when boiled with an excess of plumbic oxide (Erlenmeyer). It often spontaneously undergoes conversion into a white amorphous substance which behaves like gum arabic in water or alcohol (Linnemann, *Ann. Chem. Pharm.*, clxiii. 95, 369); this change is probably induced by some foreign body present in minute amount in the acid (comp. Caspary and Tollens, *ibid.*, clxvii. 251). Acrylic acid slowly combines with nascent hydrogen from zinc and sulphuric acid, forming propionic acid (Linnemann, *ibid.*, clxxi. 292). By heating sodic acrylate with an aqueous solution of sodic hydrate at 100° (212° F.), the elements of a molecule of water are assimilated, sodic α-hydroxypropionate being produced (comp. 1799). Acrylic acid readily unites with hydriodic acid, forming α-iodopropionic acid, $CH_2I.CH_2.COOH$ (Wislicenus); the corresponding bromo-acid is obtained by its union with bromine, but according to Linnemann (*ibid.*, clxiii. 96), the chloro-acid produced by combining it with hydrochloric acid has a lower melting point (40°·5 C.) than that obtained by the action of chlorine on α-iodopropionic acid (58° C.). It very readily unites with bromine, and forms αβ-dibromopropionic acid, much heat being developed. When fused with potassic hydrate, it furnishes a mixture of potassic formate and acetate (Erlenmeyer, *ibid.*, cxci. 376); it does not yield acetic acid, however, when merely oxidized by treatment with reagents such as nitric or chromic acid (Linnemann).

Acrylates.—Sodic acrylate, $C_3H_3O_2Na$, is an indistinctly crystalline white salt, very slightly soluble even in boiling anhydrous alcohol, but extremely soluble in water. *Plumbic acrylate*, $(C_3H_3O_2)_2Pb$, the most characteristic salt of the acid, crystallizes very readily in long glistening needles, easily soluble in water. *Argentic acrylate*, $C_3H_3O_2Ag$, the least soluble of the acrylates, also crystallizes in fine glistening needles; it is scarcely decomposed by boiling its aqueous solution.

Ethereal salts of acrylic acid have not been prepared from the acid itself, but by treating the *aβ*-dibromopropionates with nascent hydrogen (Caspary and Tollens, *loc. cit.*). *Methylic acrylate*, $C_2H_3O_2.CH_3$, is a highly pungent but not unpleasant smelling liquid, boiling at 80°—85° (176°—185° F.). *Ethylic acrylate*, $C_3H_3O_2.H_5$, also possesses a most penetrating pungent odour, and boils at 102° (215°·6 F.). *Allylic acrylate*, $C_3H_3O_2.C_3H_5$, is a liquid of unpleasant, pungent odour; it boils at 119°—124° (246°·2—255°·2 F.), but on distillation after a portion has passed over the residue suddenly becomes a jelly-like mass; on raising the temperature, however, the whole passes over. This polymerization also gradually takes place at ordinary temperatures, especially in sunlight, a hard transparent mass being formed.

(1887) ACIDS OF THE FORMULA $C_3H_5.COOH$.—No less than three of these are known—viz., crotonic acid, isocrotonic acid, and methacrylic acid.

Crotonic acid; a-methacrylic acid: $CH_3.CH{=}CH.COOH$.—Crotonic acid is formed—1. by oxidation of crotonic aldehyde (1650); 2. by dry distillation of *β*-hydroxybutyric acid (Wislicenus, 1807); 3. by heating the bromobutyric acid $CH_3.CH_2.CHBr.COOH$, with water or alkalies (1770); 4. by the action of nascent hydrogen on *a*-chlorocrotonic acid; 5. by heating isocrotonic acid; and 6. by digesting allylic iodide with an alcoholic solution of potassic cyanide, and decomposing the resulting cyanide by boiling with alkali. The formation of crotonic acid by this last method involves an isomeric change, since allylic iodide has the formula $CH_2{=}CH.CH_2I$ (Kekulé and Rinne, *Deut. chem. Ges. Ber.*, vi. 386); Pinner's experiments (*ibid.*, xii. 2053) indicate that this change is the result of the formation of hydroxybutyric acid by the addition of the elements of a molecule of water to the acid formed by the mere displacement of the iodine in allylic iodide by carboxyl, and the subsequent reversal of this reaction: $CH_3.CH(OH).CH_2.COOH = CH_3.CH{=}CH.COOH.OH_2$.

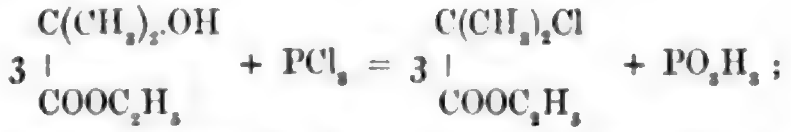
Crotonic acid crystallizes in monoclinic prisms, melting at 72° (161°·6 F.), easily soluble in water; it boils at 189° (372°·2 F.) (Kekulé, *Ann. Chem. Pharm.*, clxii. 111). By the action of nascent hydrogen, it is very slowly converted into butyric acid (Bulk). On fusion with potassic hydrate, it yields two molecules of potassic acetate, but on oxidation with either nitric or chromic acid, it furnishes only a single molecule of acetic acid, together with oxalic acid or the products of the further oxidation of this acid (Kekulé). It readily combines with hydriodic and hydrobromic acids, forming mixtures of isomeric monohaloid butyric acid derivatives (Alberti, *Deut. chem. Ges. Ber.*, ix. 1194).

Argentic crotonate, $C_4H_5O_2Ag$, is very difficultly soluble in cold water and much less soluble than argentic acetate in boiling water.

Isocrotonic or *quartenylic acid* is obtained by the action of nascent hydrogen on the chlorocrotonic acid, melting at 59°·5 (139°·1 F.), prepared from ethylic acetoacetate. It is a colourless oily liquid, of pungent odour recalling that of butyric acid; it boils at 172° (341°·6 F.), and at 25° (77° F.) has the sp. gr. 1·018. It is miscible with water in all proportions (Geuther, *Jour. pr. Chem.* [2], iii. 441). When distilled, it is partially converted into the solid isomeride above described; the same change takes place to a greater extent on heating it in sealed tubes at 170°—180° C. (Hemilian, *Ann. Chem. Pharm.*, clxxiv. 330), but the conversion is never complete (Alberti, *Deut. chem. Ges. Ber.*, ix. 1194). It combines with the haloid acids, and apparently yields only a single product; on heating the compound which it forms with hydrobromic acid with water, solid crotonic acid is obtained (Alberti). On fusion with potassic hydrate it behaves in precisely the same manner as solid crotonic acid; it is readily oxidized by a cold solution of potassic permanganate, yielding acetic, oxalic and carbonic acids (Hemilian). A number of isocrotonates have been described by Geuther.

Isocrotonic acid is usually represented by the formula $CH_2{=}CH.CH_2.COOH$ as it is isomeric with solid crotonic and β-methacrylic acids, and there are only three acids of the composition $C_3H_5.COOH$ possible according to our present theory. An acid of this formula, however, should furnish formic and propionic acids, and not acetic acid on fusion with potassic hydrate. In order to overcome this difficulty, Hemilian suggests that the isomeric change which has been shown to take place on heating also occurs when the acid is fused with potassic hydrate: but apart from the fact that the conversion into the isomeric acid is not complete even after prolonged heating (Alberti), the observation that abnormal products are also obtained when the oxidation is effected without the aid of heat by permanganate appears not to harmonize with this explanation. It is, in fact, by no means improbable that crotonic and isocrotonic acids afford another instance of the insufficiency of our present system of formulating isomerides: in other words, that both must be represented by the same formula.

Methacrylic acid; β-methacrylic acid: $CH_2{=}C(CH_3).COOH$.—This acid was first obtained, although not in a pure state, by Frankland and Duppa, by the action of phosphorous chloride on ethylic hydroxydimethacetate (dimethoxalate, 1806), &c., thus:



$$3\begin{array}{l}C(CH_3)_2.OH\\ \mid\\ COOC_2H_5\end{array} + PCl_3 = 3\begin{array}{l}C(CH_3)_2Cl\\ \mid\\ COOC_2H_5\end{array} + PO_3H_3\,;$$

$$CH_3.CCl(CH_3).COOC_2H_5 = CH_2{=}C(CH_3).COOC_2H_5 + HCl.$$

Its formation in this manner has recently been further studied by Paul (*Ann. Chem. Pharm.*, clxxxviii. 52). It is also produced by boiling with alkali the chloropyrotartaric acids obtained by combining citra- and mesaconic acids with hydrochloric acid (Prehn, *ibid.*, 42).

β-Methacrylic acid is easily soluble in water, especially if warm, and crystallizes from it in long glistening prisms which melt at 16° (60°·8 F.); it boils at 160° (320° F.), but when distilled a small portion is always converted into an amorphous (?) polymeride (Prehn). Its calcic and silver salt both crystallize well, but the baric salt is amorphous; the ethylic salt is converted into a transparent, jelly-like substance when heated (Paul). It is readily converted into isobutyric acid when submitted in cold aqueous solution to the action of sodium amalgam, whereas the isomeric acids are not in the least affected even at 100° (212° F.). On fusion with potassic hydrate, it furnishes a mixture of formate and propionate (Frankland and Duppa). It combines with hydriodic acid, forming a crystalline dimethiodacetic acid (Paul).

(1888) ACIDS OF THE FORMULA $C_4H_7.COOH$.—Four of these acids are known: α^2-dimethacrylic acid, αβ-dimethacrylic or methylcrotonic acid, angelic acid and allylacetic acid.

α^2-Dimethacrylic acid: $(CH_3)_2C{=}CH.COOH$.—This acid is produced from the hydroxyisopropacetic acid of the formula $(CH_3)_2C(OH).CH_2.COOH$, obtained by oxidizing isopropacetic acid with potassic permanganate, by distilling it with sulphuric acid. It crystallizes in monoclinic prisms, melting at 70° (158° F.) (Miller, *Deut. chem. Ges. Ber.*, xi. 1526, 2216; xii. 1542).

αβ-Dimethacrylic, methylcrotonic or *tiglic acid:* $CH_3.CH{=}C(CH_3).COOH$.—The researches of Geuther and Fröhlich and of Schmidt and Berendes (*Ann. Chem. Pharm.*, cxci. 94) have shown that this acid occurs as glyceric salt in croton oil, the oil distilled from the seeds of *Croton tiglium*. Ethereal salts derived from it are also present in oil of chamomile-flowers (*Anthemis nobilis*) (Fittig, Kopp, and Köbig, *ibid.*, cxcv. 81, 92); and it may be obtained by saponification of cevadine and cevadilline, two alkaloids extracted from the seeds of *Veratrum sabadilla* (Wright and Luff, *Jour. Chem. Soc.*, 1878, 338). It may be produced by heating ethylic methethhydroxyacetate (1807) with phosphorous trichloride, &c. (Frankland and Duppa); by dry distillation of α-methyl-β-hydroxybutyric acid (Rohrbeck); and by heating angelic acid (q.v.).

αβ-Dimethacrylic acid crystallizes in triclinic prisms, melting at 64°·5 (148°·1 F.), and boils at 198°·5 (389°·3 F.). It is difficultly soluble in cold water, but more soluble in hot, and volatilizes very readily in a current of steam. It is not altered by the action of nascent hydrogen from sodium amalgam and water. On fusion with potassic hydrate, it yields a mixture of potassic acetate and propionate. It readily combines with hydrobromic acid, forming a bromovaleric acid, probably $CH_3.CH_2.CBr(CH_3).COOH$, which crystallizes in large monoclinic prisms, melting at 86° (186°·8 F.); this acid is reduced by nascent hydrogen, and converted into a valeric acid, which is probably methethacetic acid (p. 831); when boiled with water, it is for the most part reconverted into αβ-dimethacrylic acid and hydrobromic acid: a portion, however, is resolved into α-dimethylethylene, $CH_3.CH = CH.CH_3$, carbonic anhydride and hydrobromic acid, and it almost entirely decomposes in this manner if boiled with a solution of sodic carbonate. It unites with hydriodic acid, forming an iodovaleric acid—probably $CH_3.CH_2.CI(CH_3).COOH$—melting at 86°·5 in (187°·7 F.)which is easily converted into valeric acid by reduction. It somewhat slowly combines with bromine, forming dibromovaleric acid, $CH_3.CHBr.CBr(CH_3).COOH$; this latter acid melts at 86°·5 (187°·7 F.); it readily dissolves in a cold solution of sodic carbonate, but in a very short time the liquid becomes turbid, owing to the separation of bromobutylene: $C_5H_7Br_2O_2Na = C_4H_7Br + CO_2 + NaBr$ (comp. Schmidt and Berendes; Fittig, Kopp, Köbig, and Pagenstecher, *loc. cit.*; Schmidt, *Deut. chem. Ges. Ber.*, xii. 252).

Angelic Acid.—This acid was originally obtained from the root of the archangel (*Angelica archangelica*); it has since been procured from sumbul root (*Euryangium sumbul*); from the oil distilled from the flowers of the common chamomile; from peucedanine, a neutral substance contained in the root of masterwort (*Imperatoria ostruthium*); and from laserpitin, a bitter principle extracted from the root of *Laserpitium latifolium*.* It is best prepared from archangel root (comp. Meyer and Zenner, *Ann. Chem. Pharm.*, lv. 317).

Angelic acid crystallizes in large transparent monoclinic prisms, melting at 45° (113° F.), difficultly soluble in cold, but easily in hot water; it boils at 185° (365° F.), but on distillation, a certain amount undergoes isomeric change and is converted into αβ-dimethacrylic acid, and it may be almost entirely transformed into this acid by prolonged boiling (for at least 40 hours), or by the action of concentrated sulphuric acid (Demarçay, *Compt. Rend.*, lxxxiii. 906; Fittig and Kopp, *loc. cit.*). Angelic acid is not altered by treating its solution with sodium amalgam; on fusion with potassic hydrate, it furnishes the same products as αβ-dimethacrylic acid. It combines with hydrobromic acid, forming a bromovaleric acid identical both in physical and chemical properties with that produced in a similar manner from αβ-dimethacrylic acid (q.v.), but whereas the latter acid furnishes almost the theoretical quantity of this bromo-acid, angelic acid yields at most 60—70 per cent., and another or other (perhaps isomeric) products are obtained which are not formed from the former acid (Fittig and Pagenstecher). With hydriodic acid the two acids, however, behave somewhat differently: if a mixture of either with about ten times its weight of a solution of hydriodic acid of sp. gr. 1·96 be saturated at 0° (32° F.) with hydriodic acid gas, a clear solution is obtained from which a large quantity of crystals is deposited after some hours. Both products have the composition of iodovaleric acid, $C_5H_9IO_2$, but that from αβ-dimethacrylic acid crystallizes in fine glistening plates melting at 86°·5 (187°·7 F.), whereas that from angelic acid is obtained in more compact crystals which melt at 46° (114°·8 F.), although a small quantity remains unfused until about 76° (168°·8 F.). If a less concentrated acid be employed, both these acids are formed simultaneously from angelic acid. Both furnish the same valeric acid when reduced by means of zinc and dilute sulphuric acid (Schmidt, *Deut. chem. Ges. Ber.*, xii. 252). Angelic acid combines with bromine, forming a crystalline dibromovaleric acid identical with that obtained from αβ-dimethacrylic acid (q.v.), but whereas the latter yields almost the theoretical amount of this dibromo-acid, angelic acid furnishes only about 70 per cent. of the theoretical quantity, an oily (? isomeric) compound being also produced. When submitted to the action of nascent hydrogen, the dibromide from angelic acid is deprived of its bromine and completely converted into αβ-dimethacrylic acid, and according to Demarçay (*Compt. Rend.*, lxxx. 1400) a similar change is effected on distilling the dibromo-acid (Fittig and Pagenstecher, and Schmidt, *loc. cit.*).

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* The nature of the substances in archangel and sumbul roots which furnish angelic acid when decomposed by alkali, &c., is not known. Chamomile oil, according to Demarçay (*Compt. Rend.*, lxxvii. 360), chiefly consists of butylic and amylic angelate and valerate, but according to the more recent researches of Fittig and Köbig, who have examined specimens obtained at very different times, it consists of isobutylic isobutyrate, isobutylic angelate, and the isoamylic, isohexylic and anthemylic salts of angelic and αβ-dimethacrylic acids, and does not contain an appreciable amount of valeric compounds (comp. Schmidt, *loc. cit.*). ***Peucedanine*** has the composition $C_{12}H_{12}O_3$, and yields potassic angelate and oreoselin, $C_7H_6O_2$, on saponification with potassic hydrate. ***Laserpitin*** has the formula $C_{24}H_{36}O_7$, and yields potassic angelate and laserol $C_{14}H_{22}O_4$ when similarly treated.

Angelic and αβdimethacrylic acids therefore afford another instance of isomerism which cannot be expressed by our present system of notation: the fact that both acids furnish the same dibromovaleric acid when combined with bromine being one which necessarily involves their representation by the same formula.

Angelates and *αβ-Dimethacrylates.*—The salts of the two acids differ very considerably. *Calcic angelate*, $(C_5H_7O_2)_2Ca + 2OH_2$, is much less soluble in hot than in cold water, and if a cold saturated solution be enclosed in a tube and heated in the water bath magnificent long needle-like crystals begin to separate at a temperature of 35°—40° (95°—104° F.), and at 60°—70° (140°—158° F.) the liquid is entirely converted into a stiff pasty mass. 100 parts of solution saturated at 17°·5 (63°·5 F.) contain 23 pts. of the anhydrous salt. *Calcic αβ-dimethacrylate*, $(C_5H_7O_2)_2Ca + 3OH_2$, forms white pasty crystals much more soluble in hot than cold water; 100 pts. of a solution saturated at 17° (62°·6 F.) contain 6·05 pts. anhydrous salt. *Baric angelate*, $(C_5H_7O_2)_2Ba + 4·5OH_2$, is very soluble, and can scarcely be obtained in isolated crystals. *Baric αβ-dimethacrylate*, $(C_5H_7O_2)_2Ba + 4OH_2$, is more soluble than the calcic salt, but much less soluble than baric angelate; it forms small prismatic crystals. *Potassic angelate* is a very soluble deliquescent salt. *Potassic αβ-dimethacrylate* readily crystallizes in bundles of anhydrous needles, and does not deliquesce. *Argentic angelate* separates from boiling water in feathery crystals; *argentic αβ-dimethacrylate* is a similar salt, but less soluble (Fittig and Kopp).

Allylacetic acid, $C_3H_5.CH_2.COOH$, is a colourless oil, boiling at 182° (359°·6 F.) (Zeidler, *Ann. Chem. Pharm.*, clxxxvii. 30).

(1889) ACIDS OF THE FORMULA $C_5H_9.COOH$.—Three of these acids are known—hydrosorbic acid, *a*-isopropylacrylic or pyroterebic acid, and *a*-methyl-*β*-ethacrylic or ethylcrotonic acid.

Hydrosorbic or (?) *a-propylacrylic acid*, $C_5H_9.COOH$, is readily obtained by digesting an aqueous solution of sorbic acid, $C_5H_7.COOH$, at the ordinary temperature with sodium amalgam. It is liquid even at − 18° (− 4° F.), and at 19° (66°·2 F.) has the sp. gr. ·969; it boils at 208°·5 (406°·4 F.); it is only slightly soluble in water, but easily dissolves in alcohol and ether. Hydrosorbic acid is not altered by nascent hydrogen; on fusion with potassic hydrate, it yields a mixture of potassic acetate and normal butyrate. It combines with bromine with great readiness, forming a non-crystalline dibromocaproic acid, $C_5H_9Br_2.COOH$, which yields sorbic acid on treatment with an alcoholic solution of potassic hydrate, but which, if heated with water at 100° (212° F.), is converted into bromohydrosorbic acid, which then gradually decomposes, partly into sorbic and partly into hydroxyhydrosorbic acid. It also very readily unites with hydrobromic and hydriodic acids, forming liquid bromo- and iodocaproic acids, which furnish normal caproic acid on reduction. The bromo-acid yields hydrosorbic and hydroxycaproic acid when decomposed by water or sodic carbonate solution (Fittig and Barringer, *Ann. Chem. Pharm.*, clxi. 309; Kachel and Fittig, *ibid.*, clxviii. 289; Fittig and Mielck, *ibid.*, clxxx. 52; Fittig, Stahl, Landsberg and Engelhorn, *ibid.* cc. 42, 93; Menschutkin, *Deut. chem. Ges. Ber.*, xiii. 163).

a-Isopropylacrylic or *pyroterebic acid*, $C_3H_7^{\beta}.CH{=}CH.COOH$, is produced by dry distillation of terebic acid. According to recent experiments of Bredt and Fittig (*ibid.*, cc. 58, 259), however, the product thus obtained is not, as has been supposed, the pure acid, but a mixture of a relatively small quantity of the acid with a dehydro compound—so-called *lactone* (see coumarin)—of the formula $C_6H_{10}O_2$. If it be dissolved in water, the solution digested with excess of calcic carbonate, then distilled, and the distillate saturated with potassic carbonate, the lactone separates as an oily layer. The acid is obtained on evaporating the residue from the retort and treating the resulting salt with hydrochloric acid, when it separates as an oil much less soluble in water than the lactone.

The lactone is a colourless, perfectly neutral liquid, easily soluble in water; it boils at 206° (402°·8 F.). When boiled with a concentrated solution of baric hydrate, it is converted into baric hydroxyisocaproate.

Pyroterebic acid appears to combine with gaseous hydrobromic acid to form a crystalline bromisocaproic acid; but the aqueous acid at once converts it into the lactone. With bromine, it forms a dibromisocaproic acid melting at 99° (210°·2 F.).

a-Methyl-β-ethacrylic or *ethylcrotonic acid*, $CH_3.CH{=}C(C_2H_5).COOH$, is produced as ethylic salt by distilling ethylic diethhydroxyacetate (diethoxalate) with phosphorous trichloride (Frankland and Duppa; comp. Fittig and Howe, *ibid.*, cc. 21). It crystallizes very readily in large square prisms, very slightly soluble in water, melting at about 41° (105°·8 F.), and sublimes even at ordinary temperatures; it boils at 209° (408°·2 F.). On fusion with potassic hydrate, it yields a mixture of potassic acetate and normal butyrate. It combines, although very slowly, with hydrobromic acid when treated with a very concentrated aqueous solution of the acid. The resulting bromodiethacetic acid melts at 25°; on reduction, it yields an acid which is probably diethacetic acid; when heated with water at 100° (212° F.), it is for the most part decomposed into ethylcrotonic acid and hydrobromic acid; but if it be dissolved in water, and a slight excess of sodic carbonate be then added, the resulting sodic salt rapidly decomposes chiefly into amylene (b. p. 36° C.), carbonic anhydride, and sodic bromide. The dibromo-acid formed by combining ethylcrotonic acid with bromine (m. p. 80°·5 C.) behaves similarly (Fittig and Howe).

Each of the three acids above described furnishes characteristic salts.

Acids which very closely resemble, if they are not identical with, ethylcrotonic and pyroterebic acids respectively, have been obtained by Pinner and Lagermarck (comp. *Deut. chem. Ges. Ber.*, x. 1052; xii. 854).

(1890) HIGHER ACIDS OF THE ACRYLIC SERIES.—Our knowledge of the acids containing more than six atoms of carbon is extremely imperfect, oleic acid being the only one to which even a moderate amount of attention has been paid.

Teracrylic acid, $C_7H_{12}O_2$.—This acid (1877) is a colourless liquid of peculiar not unpleasant odour, boiling at 216°—218° (420°·8—424°·4 F.). Its calcic salt, $(C_7H_{11}O_2)_2Ca + 5OH_2$, is easily soluble in water, and crystallizes in long transparent, efflorescent needles. Like many other acids of the series, teracrylic acid readily undergoes isomeric change under certain circumstances, especially on heating its potassic salt with a concentrated potassic hydrate solution on the water-bath: the isomeride has a cymene-like odour, and furnishes a calcic salt crystallizing in long needles, less soluble in hot than in cold water (Krafft, *Deut. chem. Ges. Ber.*, x. 1659).

Damaluric acid, (?) $C_7H_{12}O_2$, according to Städeler (*Ann. Chem. Pharm.*, lxxv. 27), is a volatile acid present in cows' and horses' urine (comp. Werner, *Zeits. Chem.* [2], iv. 413).

Moringic acid, (?) $C_{15}H_{28}O_2$.—According to Walter (*Ann. Chem. Pharm.*, lx. 271), this acid is obtained, together with palmitic and other acids of the acetic series, by the saponification of oil of ben (*Moringa Nux Behen*).

Cimicic acid, $C_{15}H_{28}O_2$, occurs in the free state in *Rhaphigaster punctipennis*, an insect of the order *Cimex*. It is a crystalline substance of peculiar rancid odour, melting at 44° (111°·2 F.), insoluble in water (Carius, *ibid.*, cxiv. 147).

Hypogæic acid, $C_{16}H_{30}O_2$, is obtained on saponification of oil of earth-nut (*Arachis hypogæa*) (Gössmann and Sheven, *ibid.*, xciv. 230; xcix. 305), and is perhaps identical with physetoleic acid from sperm oil (Schröder, cxliii. 22; Hofstädter, *ibid.*, xci. 177). Hypogæic acid crystallizes in colourless needles, melting at 34° (93°·2 F.); it gradually oxidizes on exposure to the air. On treatment with nitrous acid, or when heated with nitric acid, it is converted into *gaïdic acid*, a body of the same empirical composition, and probably of the same molecular weight. Gaïdic acid melts at 39° (102°·2 F.), and does not oxidize on exposure to the air. Hypogæic acid decomposes on distillation, being partially converted into sebacic acid, $C_8H_{16}(COOH)_2$; gaïdic acid may be volatilized unchanged. Physetoleic acid is said to melt at 30° (86° F.). Both hypogæic and gaïdic acids combine with a single molecular proportion of bromine.

Oleic acid, $C_{18}H_{34}O_2$.—The normal glyceride of this acid (*olein*),*

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* The oils which contain principally glyceric oleate belong to the class of *non-drying oils*; the so-called *drying oils*, such as hemp, linseed and poppy oils, chiefly consist of the glyceride of *linoleic acid*. This acid is said to have the formula $C_{16}H_{28}O_2$, and would seem therefore to bear a very simple relation to hypogæic and palmitic acids; but at present even its composition cannot be regarded as established.

$C_3H_5(O.C_{18}H_{33}O_2)_3$, is present in most natural fats and fatty oils, being especially abundant in the latter; it was discovered by Chevreul in 1811, but first obtained pure by Gottlieb, who established its formula, in 1846. To prepare pure oleic acid, an oil rich in olein, such as olive or almond oil, is saponified with potassic or sodic hydrate; or the crude oleic acid obtained as a byeproduct in the manufacture of stearic acid is treated in a similar manner; the resulting salt is decomposed by dilute hydrochloric acid, and the separated mixture of fatty acids is digested for some hours at 100° (212° F.) with finely powdered plumbic oxide, sufficient of the latter being used to saturate only the greater part of the oleic acid. The mixture of lead salts thus obtained is extracted with cold ether, which dissolves only the oleate, leaving the salt of the solid fatty acid undissolved. The ethereal liquid is shaken with an excess of hydrochloric acid, and the upper layer is then separated and the ether removed by distillation. The acid thus prepared is still contaminated with products of oxidation and colouring matter, to separate which it is cooled down to about − 7° (19°.4 F.), when it solidifies to a crystalline mass, which is pressed between folds of bibulous paper, or drained on a vacuum filter; by repeatedly melting, cooling, and pressing the crystallized portion, at last with the addition of a little alcohol, the impurities are completely removed.

Oleic acid crystallizes from alcohol in brilliant white needles, melting at 14° (57°·2 F.); it is insoluble in water, but very soluble in alcohol and ether. The solid acid does not alter on exposure to air, but the liquid acid rapidly absorbs oxygen, acquiring a yellow colour and rancid odour. It volatilizes in a vacuum almost, if not entirely, without decomposition; but when distilled in the ordinary manner, it breaks up into lower acids of the acetic series, sebacic acid, and hydrocarbons. On oxidation with nitric acid, it yields a complex mixture of oxidation products, consisting of lower acids of the acetic series, succinic, suberic and azelaic acids, &c. Oleic acid combines with a single molecular proportion of bromine, forming an oily dibromide, $C_{18}H_{34}Br_2O_2$, which yields oleic acid on treatment with nascent hydrogen (Overbeck, *ibid.*, cxl. 39).

By the action of nitrous acid, oleic acid is converted into an isomeride of higher melting point, *elaïdic acid.* To prepare this substance, the nitrous fumes evolved on heating starch, sugar, or arsenious anhydride with nitric acid are passed for a few minutes only into pure cooled oleic acid; after some time, the elaïdic acid crystallizes out, and may be purified by washing with water and crystallization from alcohol. The amount obtained in this manner is not large, however (Overbeck). It forms fine pearly laminæ, melting at 45° (113° F.); it distils unchanged in an atmosphere free from oxygen, but, like oleic acid, it gradually absorbs oxygen when in a fused state. Both oleic and elaïdic acids yield a mixture of acetate and palmitate on fusion with potassic hydrate (Varrentrapp, *ibid.*, xxxv., 196): $C_{18}H_{34}O_2 + 2KHO = C_{16}H_{31}KO_2 + C_2H_3KO_2 + H_2$. Elaïdic acid combines with a single molecular proportion of bromine.

This mode of decomposition would appear to favour the conclusion that they are both acids of the formula $C_{15}H_{31}.CH=CH.COOH$; but such an assumption is to a great extent negatived by the observation that stearolic acid (1914)—which is formed by the withdrawal of two atoms of hydrogen from oleic acid—yields stearoxylic acid when oxidized, and that this latter on further oxidation is resolved into azelaic acid, $C_7H_{14}(COOH)_2$, and nonylic acid, $C_8H_{17}.COOH$. The most probable interpretation of this behaviour is afforded by assigning the following formulæ to these acids:

$$\underset{\text{Stearolic acid.}}{C_8H_{17}.C\equiv C.C_7H_{14}.COOH} \qquad \underset{\text{Stearoxylic acid.}}{C_8H_{17}.CO.\ CO.\ C_7H_{14}.COOH}$$

Metallic Oleates.—An alcoholic solution of oleic acid is said to be without action on litmus. Little is known of the metallic oleates, as it is difficult to prepare them in a pure state on account of the tendency of oleic acid to form acid and basic as well as normal salts. The alkali metal salts only are soluble in water; the others are soluble in alcohol, and some also in ether. *Baric oleate*, $(C_{18}H_{33}O_2)_2Ba$, separates from a boiling alcoholic solution on cooling as a bulky white crystalline powder.

The salts of elaïdic acid crystallize more readily, the sodic salt separating from alcohol in large glistening plates.

Oleins.—The only ethereal salts of oleic acid which have been investigated are the glyceric oleates or oleins, which, as Berthelot has shown, may be prepared by heating glycerin with oleic acid at 200°—240° (392°—464° F.), but it is scarcely possible to obtain any of them in a pure state; they are represented by the following formulæ:

$$C_3H_5\begin{cases}O.C_{18}H_{33}O_2\\OH\\OH\end{cases}\qquad C_3H_5\begin{cases}O.C_{18}H_{33}O_2\\O.C_{18}H_{33}O_2\\OH\end{cases}\qquad C_3H_5\begin{cases}O.C_{18}H_{33}O_2\\O.C_{18}H_{33}O_2\\O.C_{18}H_{33}O_2\end{cases}$$

Monolein. Diolein. Triolein.

Only triolein (olein) appears to occur naturally. By treatment with nitrous acid, this compound is converted into the isomeric *elaïdin*, which melts at 32°—38° (89°·6—100°·4 F.), olein being liquid at temperatures above 0° (32° F.).

Doeglic acid, $C_{19}H_{36}O_2$.—According to Scharling (*ibid.*, xcvi. 236; *Jahresb.*, 1847—48, 567), the oil from the doegling, or bottle-nosed whale, contains an ethereal salt of this acid, analogous to spermaceti; the acid itself is very similar to oleic acid.

Brassic or *Erucic acid*, $C_{22}H_{42}O_2$.—The glyceride of this acid is the chief constituent of rape or colza oil, the oil expressed from the seeds of *Brassica campestris*, var. *oleifera*, and also of the oil of black and yellow mustard-seed. To prepare the acid, rape oil is saponified with litharge, and the resulting plaster is thoroughly extracted with ether; the residue, consisting of plumbic erucate, is treated with hydrochloric acid, and the acid thus formed purified by crystallization from alcohol (Hauseknecht, *Ann. Chem. Pharm.*, cxliii. 40). It crystallizes in long, thin, brilliant white needles, melting at 33°—34°, insoluble in water, but very soluble in ether and still more so in alcohol. It gradually oxidizes on exposure to the air. It is not altered by nitrous acid. Erucic acid combines with bromine to form a dibromide, which is converted again into the parent acid when submitted to the action of nascent hydrogen (Otto, *Ann. Chem. Pharm.*, cxxxv. 226). According to Otto, erucic acid does not furnish any acetate on fusion with potassic hydrate.

(1891) HALOID DERIVATIVES OF THE ACIDS OF THE ACRYLIC SERIES.—A number of these have been obtained chiefly by methods analogous with those which are employed in preparing haloid derivatives of the olefines—*i.e.*, by withdrawing the elements of a molecule of haloid acid from di- or more highly substituted haloid derivatives of acids of the acetic series, or by combining acids isologous with the acids of the acrylic series with the halogens or haloid acids. Demarçay has prepared several chlorinated acids by acting on methyl- and other derivatives of ethylic acetoacetate of the form $CH_3.CO.CH(C_nH_{2n+1}).COOC_2H_5$ and $CH_3.CO.C(C_nH_{2n+1})_2.COOC_2H_5$ with phosphoric pentachloride and heating the product (*Compt. Rend.*, lxxxiv. 1087). At present, however, we have little knowledge of any except those derived from acrylic acid.

(1892) CHLORACRYLIC ACIDS; *α-Chloracrylic acid*,* $CHCl{=}CH.COOH$, is best obtained by acting on ethylic trichlorolactate (1804) with nascent hydrogen from zinc and hydrochloric acid; it is also produced when chloralide (1805) is similarly treated (Wallach, *Ann. Chem. Pharm.*, cxciii. 28; *Deut. chem. Ges. Ber.*, x. 569, 2131). It crytallizes in plates melting at 85° (185° F.), moderately soluble in water; when boiled with a solution of baric hydrate, it yields malonic acid (Pinner).

β-Chloracrylic acid, $CH_2{=}CCl.COOH$, is produced on heating ethylic αβ-dichloropropionate, $CH_2Cl.CHCl.COOC_2H_5$, with a solution of baric hydrate. It crystallizes in thin needles grouped in bundles, which melt at 65° (149° F.); when heated above the melting-point, it gradually becomes solid and insoluble in water. It is converted into carbacetoxylic acid (1820) when digested in aqueous solution with argentic hydrate (Werigo and Werner, *ibid.* x. 1499; *Ann. Chem. Pharm.*, clxx. 170).

An acid, which from its mode of formation should possess the same formula, is obtained on boiling the silver salt of β^2-dichloropropionic acid (1769) with water, but it is said to be liquid. This acid readily combines with hydrochloric acid, forming β^2-dichloropropionic acid; and by the action of nascent hydrogen in acid solution, it is converted into propionic acid (Otto and Beckurts, *Deut. chem. Ges. Ber.*, x. 1948).

α^2-Dichloracrylic acid, $CCl_2{=}CH.COOH$.—According to Wallach (*Ann. Chem. Pharm*, cxciii. 19), this acid is formed on reducing chloralid with nascent hydrogen. It crystallizes in fine needles or prisms, melting at 77° (170°·6 F.), but if heated to above the melting-point and then quickly cooled and again fused it melts at 64° (147°·2 F.). It is remarkable that it does not combine with bromine even at 200° (392° F.). When gently heated in aqueous solution with baric hydrate, it is apparently converted into chloropropiolic acid, $CCl{\equiv}C.COOH$, which, however, very readily undergoes decomposition into carbonic anhydride and spontaneously inflammable chloracetylene (*Deut. chem. Ges. Ber.*, xii. 57). Bennett and Hill (*ibid.*, xii. 655) have obtained an isomeric dichloracrylic acid, which probably therefore has the formula $CHCl{=}CCl.COOH$, by the action of alkalies on mucochloric acid (1923). It crystallizes in very volatile small rhombic prisms, melting at 86° (186°·6 F.). When boiled with baric hydrate solution, it behaves in precisely the same manner as the corresponding dibromo-acid.

(1893) BROMACRYLIC ACIDS; *α-Bromacrylic acid*, $CHBr{=}CH.COOH$, obtained by the action of nascent hydrogen on tribromolactic chloralid (p. 894) crystallizes in fine needles, melting at 116° (240°·8 F.). It combines with bromine (Wallach).

β-Bromacrylic acid, $CH_2{=}CBr.COOH$, prepared from β^2-dibromopropionic acid,† crystallizes in rectangular plates melting at 70° (158° F.)

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* This acid is usually termed the β-acid and the isomeric acid the α-acid; it is here termed the α-acid in accordance with the system indicated on p. 861 (foot-note), and as being a member of the α-series of di-derivatives of ethylene.

† In preparing this acid, an amorphous insoluble colloidal substance of the empirical formula $C_3H_4O_2$ is frequently produced; in fact, the acrylic compounds generally are highly prone to undergo conversion into bodies of this kind (comp. Wagner and Tollens, *ibid.*, clxxi. 355).

(Phillipi and Tollens, *Ann. Chem. Pharm.*, clxxi, 333). According to Wagner and Tollens (*ibid.*, clxxi. 340), αβ-dibromopropionic acid yields a bromacrylic acid which resembles that from the β^2-acid in every particular except that the potassic salt of that derived from the former crystallizes in rhombic tablets, and the potassic salt of that derived from the latter in rectangular plates. The acids from both sources combine with hydrobromic acid, forming αβ-dibromopropionic acid.

α^2-Dibromacrylic acid, $CBr_2{=}CH.COOH$, formed by boiling an aqueous solution of tribromosuccinic acid (Fittig and Petri, *ibid.*, cxcv. 70), and by combining bromopropiolic acid with hydrobromic acid (Hill), crystallizes from water in large glistening plates, melting at 86° (186°·8 F.).

αβ-Dibromacrylic acid, $CHBr{=}CBr.COOH$.—An acid which probably has this formula is obtained by decomposing mucobromic acid (1923) with baric hydrate solution: $C_4H_2Br_2O_3 + OH_2 = C_3H_2Br_2O_2 + HCOOH$ (Jackson and Hill, *Deut. chem. Ges. Ber.*, xi. 1674; xi. 658). It crystallizes from ether in small rhombic prisms of the same melting-point as the α^2-acid. By boiling with baric hydrate solution, it is resolved into hydrobromic acid and bromopropiolic acid, $CBr{\equiv}C.COOH$; the latter, however, is partially converted into bromacetylene and carbonic anhydride, and partially into malonic acid.

(1894) HALOID DERIVATIVES OF THE ACIDS OF THE FORMULA $C_3H_5.COOH$.—Two isomeric monochlorocrotonic acids are obtained by the action of phosphoric pentachloride on ethylic acetoacetate and treatment of the product with water, &c. (p. 910); one of these volatilizes readily, the other with difficulty, in a current of steam. The less volatile or α-chlorocrotonic acid crystallizes in monoclinic prisms melting at 94°·5 (202°·1 F.), and boiling at about 212° (413°·6 F.). It is easily soluble in hot water, alcohol or ether. According to Geuther, it loses the elements of a molecule of hydrochloric acid when heated with potassic hydrate solution, being converted into tetrolic acid (comp. 1910). As it is converted into crotonic acid (1887) by the action of nascent hydrogen from sodium amalgam, α-chlorocrotonic acid has the formula $CH_3.CCl{=}CH.COOH$.

The isomeric β-chlorocrotonic acid, termed by Geuther chloroquartenylic acid, is difficultly soluble even in hot water; it melts at 59°·5 (139°·1 F.), and boils at 195° (383° F.). On treatment with nascent hydrogen, it is converted into isocrotonic acid. It does not yield tetrolic acid when treated with potassic hydrate solution. It has already been pointed out (p. 958) that crotonic and isocrotonic acids probably have the same formula, and if this be the case we must represent these two chlorocrotonic acids by the same formula.

A third chlorocrotonic acid is obtained by reducing the trichlorobutyric acid formed on oxidation of trichlorotetraldehydrol (1632; Sarnow), or by the action of potassic cyanide on an alcoholic solution of the latter compound (Wallach, *ibid.*, x. 1529). Although somewhat similar in appearance to the α-acid, it melts at 97°·5 F. (207°·5 F.), and does not yield tetrolic acid when submitted to the action of potassic hydrate (Kahlbaum, *ibid.*, xii. 2335; comp. 1900).

Chloromethacrylic acid, $CHCl{=}C(CH_3).COOH$, is one of the products of the action of chlorine on citra- and mesaconic acids (1898). It crystallizes from water in long colourless needles melting at 59° (138°·2 F.). The trichlorobutyric acid formed by combining this acid with chlorine yields dichloromethacrylic acid, $CCl_2{=}C(CH_3).COOH$, when decomposed by alkalies (Gottlieb, Morawski, *Jour. pr. Chem.* [2], xii., 1, 369).

Bromomethacrylic acid, $CHBr{=}C(CH_3).COOH$, is obtained in a similar manner by boiling the aqueous solution of the dibromo-acids formed by combining citra- and mesaconic acids with bromine (comp. Fittig and Landolt, *Ann. Chem. Pharm.*, clxxxviii. 84; Morawski, *loc. cit.*). It crystallizes in long flat needles, melting at 65° (149° F.); it is converted into isobutyric acid by the action of nascent hydrogen from sodium amalgam. Di- and tribromomethacrylic acids have been prepared by Cahours (*Ann. Chem. Pharm.*, Sup. ii. 349).

A bromocrotonic acid is formed by the action of alkalies on the dibromobutyric acid resulting from the combination of crotonic acid with bromine; at the same time, however, a portion of the acid is decomposed into bromopropylene, hydrobromic acid, and carbonic anhydride (Körner, *ibid.*, cxxxvii. 234).

§ VII. Acids of the $C_nH_{2n-2}(COOH)_2$ Series.

(1895) The following terms of this series are known:

Maleic acid	$C_2H_2(COOH)_2$
Fumaric acid	
Citraconic acid	$C_3H_4(COOH)_2$
Mesaconic acid	
Itaconic acid	
Crotaconic acid	
Hydromuconic acid	$C_4H_6(COOH)_2$
Xeronic acid	$C_6H_{10}(COOH)$
Hexahydrophthalic acid	
Camphoric acid	$C_8H_{14}(COOH)_2$

Those of the formula $C_2H_2(COOH)_2$ and $C_3H_4(COOH)_2$ are strictly homologous, but the remaining acids represent very different types.

(1896) **Fumaric Acid:** $C_4H_4O_8$=COOH.CH=CH.COOH.—Fumaric acid occurs naturally in a number of plants, as Fumitory (*Fumaria officinalis*), *Corydalis bulbosa*, *Lichen islandicus*, several species of *Boletus*, &c. It is produced on boiling malic acid with fuming hydrochloric or hydrobromic acid (comp. 1855), but is most conveniently prepared by heating this acid at about 140°—150° (284°—302° F.) for a considerable time until water is no longer given off. Werigo and Tanatar have shown (*ibid.*, clxxiv. 367) that a small quantity of fumaric acid is formed together with optically inactive malic acid on heating ethylic $\alpha\beta$-dichloropropionate with an alcoholic solution of potassic cyanide. According to Carius, "trichlorophenomalic acid," obtained by the action of chlorous acid on benzene, yields fumaric acid when decomposed by boiling with baric hydrate solution (*Deut. chem. Ges. Ber.*, iv. 928); if, as Krafft has stated (foot-note, p. 795), "trichlorophenomalic acid" is none other than trichloroquinol, this method of formation is of especial interest.

Fumaric acid crystallizes in colourless prisms, sparingly soluble in cold, but readily in hot water; if heated in a narrow glass tube, the greater part sublimes without melting at about 250°—280° (482°—536° F.), but if distilled, it for the most part decomposes into water and maleic anhydride. By heating it with a large quantity of water at 150° (302° F.), the greater part is converted into inactive maleic acid (comp. p. 941); on the other hand, if maleic acid is heated with a small quantity of water at 180° (356° F.), it is almost completely converted into fumaric acid (Jungfleisch, *Bull. Soc. Chem.*, xxx. 147).

(1897) MALEIC ACID: $C_4H_4O_8$=COOH.CH=CH.COOH.—This acid is formed together with fumaric acid on distilling malic acid (1863); and also on heating argentic succinate mixed with sand at about 108° (226°·4 F.) (Bourgoin). To prepare the pure acid, malic acid is completely converted into maleic anhydride by repeated distillation, and the latter is then boiled with water.

Maleic acid is easily soluble even in cold water, from which it crystallizes in oblique rhombic prisms melting at 130° (266° F.); it decomposes on distillation into water and maleic anhydride, Maleic acid exhibits the greatest tendency to undergo conversion into the isomeric fumaric acid, this change taking place when it is heated for some time at about its melting-point, or when it is boiled with dilute nitric or sulphuric acid. If the finely powdered acid be shaken with a cold saturated solution of hydrobromic acid, it rapidly dissolves, but almost immediately crystals begin to separate, and in a few minutes the liquid solidifies to a pasty mass; if, after removing the mother-liquor, the mass of crystals is treated with cold water, a part dissolves, leaving a residue of fumaric acid, that which has dissolved consisting of monobromosuccinic acid. Precisely similar results are obtained with maleic anhydride. In both cases, the two products are obtained in a constant proportion even when very different amounts of hydrobromic acid are employed, and it would almost appear that a compound of the formula $COOH.C_2H_2.CO.O.CO.C_2H_3Br.COOH$ is produced, which, however, is at once decomposed by pure water (comp. 1855); Fittig and Dorn, *Ann. Chem. Pharm.*, clxxxviii. 87).

Maleic and fumaric acids readily combine with nascent hydrogen, being both converted into succinic acid; their behaviour with bromine and hydrobromic acid has already been described (1855); the same products are obtained from both on electrolysis of solutions of their potassic salts—viz., acetylene, hydrogen and potassic carbonate. Fumaric acid is converted into fumaric chloride, $C_2H_2(COCl)_2$, by phosphoric pentachloride; maleic chloride is not known. The two acids differ in crystalline form, amount of water of crystallization, and solubility. Maleic acid is not precipitated by argentic nitrate, but a neutral maleate yields a white precipitate which becomes crystalline on standing;

even very dilute solutions of fumaric acid, however, furnish a white amorphous precipitate of argentic fumarate. Ferric salts do not produce a precipitate in neutral solutions of either acid.

Ethereal salts of fumaric acid may be prepared by the ordinary methods and by distilling the corresponding malates. *Methylic fumarate* is a crystalline body; it melts at 102° (215°·6 F.), and boils at 192° (377°·6 F.). *Ethylic fumarate* is an oily liquid; it boils at 218° (424°·4 F.). Both combine readily with bromine. Corresponding maleates are formed by acting on argentic maleate with methylic and ethylic iodide *free from iodine.* Both are liquids; *methylic maleate* boils at 205° (401° F.); *ethylic maleate* at 225° (437° F.). On merely warming with a little iodine, they are readily and completely converted into the corresponding fumarates (Anschütz, *Deut. chem. Ges. Ber.*, xii. 22, 80).

Maleic anhydride, $C_2H_2(C_2O_2)O$.—Both maleic and fumaric acid are converted into this compound on distillation; it is a crystalline substance melting at 60° (140° F.) and boiling at 196° (384°·8 F.). Its vapour density corresponds with the formula $C_4H_2O_3$ (Huebner and Schreiber, *Zeits. Chem.* [2], vii. 712).

(1898) PYROCITRIC ACIDS.—No less than four isomeric acids of the formula $C_3H_4(COOH)_2$ are known, three of which—*citra-*, *ita-* and *mesaconic acid*—are obtained more or less directly from citric acid.

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Citraconic acid, $CH_3.C(COOH){=}CH.COOH$, is prepared from citraconic anhydride, which is obtained by distilling citric acid. Ordinary citric acid is distilled as rapidly as possible in quantities of not more than 250 grams, and the oily product is rectified two or three times, the portion boiling at about 214° (417°·2 F.) being collected apart; 1000 grams of citric acid treated in this manner yield a little over 200 grams of the anhydride* (comp. Fittig and Landolt, *Ann. Chem. Pharm.*, clxxxviii. 71). If the anhydride thus obtained is mixed with a small quantity of water, it is soon converted into a crystalline mass of citraconic acid.†

Mesaconic acid, $CH_3.C(COOH){=}CH.COOH$, is prepared from citraconic anhydride by boiling down a mixture of two parts of the anhydride, two parts water, and three parts of nitric acid of sp. gr. 1·074 (one part ordinary acid and four parts water), until red fumes are evolved; the acid which separates from the solution on cooling requires only to be once recrystallized from water. A good yield of this acid may also be obtained by evaporating a solution of citraconic acid in concentrated hydrochloric acid to a small bulk, and recrystallizing the product from water (Fittig and Landolt).

Itaconic acid, $CH_2{=}C(COOH).CH_2.COOH$, may be obtained in almost theoretical quantity by heating pure citraconic anhydride with 2—3 volumes of water in a closed vessel for 6—8 hours at 150° (302° F.); the solution is set aside to crystallize, and the filtrate from the crystals is afterwards concentrated, and when it no longer deposits crystals of the acid, it is mixed with a small quantity of water, and again heated as before (Fittig and Landolt).

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* Citraconic anhydride is not the immediate product of decomposition. The citric acid is in the first place resolved into water and aconitic acid; this latter then breaks up into carbonic anhydride and itaconic acid, which, however, undergoes decomposition and yields water and citraconic anhydride. A considerable quantity of acetone is also produced, and even the citraconic anhydride does not distil entirely unchanged (see Xeronic acid; 1903).

† According to Engelhardt (*Ann. Chem. Pharm.*, lxx. 246), a small quantity of citraconic acid (anhydride) is produced on dry distillation of lactic acid. It is also formed in small quantity by the decomposition of pyruvic acid (Bottinger, *Deut. chem. Ges. Ber.*, ix. 1823).

Citraconic acid crystallizes in large glistening four-sided prisms, melting at 80° (176° F.), extremely soluble in water; when carefully heated in small quantity at about 100° (212° F.) it is converted into itaconic acid, but on distillation it is resolved into the anhydride and water. It appears to be appreciably volatile with vapour of water; probably, however, it does not volatilize as such, but as the anhydride (Fittig).

Mesaconic acid crystallizes in fine white needles, melting at 202° (395°·6), soluble in 38 parts of water at 14° (57°·2 F.); it sublimes undecomposed at a temperature a few degrees above its melting-point, but is resolved into citraconic anhydride and water on distillation.

Itaconic acid crystallizes in rhombic prisms, melting at 161° (321°·8 F.), at about which temperature it sublimes unchanged, but it also is resolved into citraconic anhydride and water on distillation; it dissolves in 17 parts of water at 10° (50° F.).

Citra-, ita- and mesaconic acids readily combine with nascent hydrogen, and on treatment of their aqueous solutions with sodium amalgam or on digesting their alcoholic solutions with zinc dust, they are each converted into methylsuccinic (pyrotartaric) acid (1847; comp. Böttinger, *Deut. chem. Ges. Ber.*, ix. 1821), $CH_3.CH(COOH).CH_2.COOH$. They combine with bromine, however, to form isomeric dibromo-acids of the formula $C_3H_4Br_2(COOH)_2$ (comp. p. 935). The action of chlorine is similar to that of bromine, but the resulting dichloro-acids are highly unstable, and when formed in presence of water exchange one-half their chlorine for hydroxyl; citra- and mesaconic acids are thus converted into *chlorocitramalic acid*, $C_3H_4Cl(OH)(COOH)_2$; itaconic acid forming the isomeric *chloritamalic acid*. These same products appear to be formed by the combination of the pyrocitric acids with hypochlorous acid. The action of chlorine on an aqueous solution of sodic citraconate takes place with considerable energy, much heat being developed, and besides chlorocitramalic acid, trichlorobutyric acid and trichloracetone are obtained in considerable quantity as end-products of the reaction. Doubtless a part only of the dichloro-acid, which is first produced, is converted into chlorocitramalic acid, a part being resolved into chlorocrotonic acid, which combines with chlorine forming trichlorobutyric acid; the trichloracetone is probably a product of the action of chlorine on chlorocitramalic acid. Sodic mesaconate and itaconate, which are attacked with much less energy, furnish an almost pure product* (Morawski, *Jour. pr. Chem.* [2], vii. 158; x. 88; xi. 450; xii. 369; Gottlieb, *ibid.*, xii.). Similar bye-products appear to be formed by the action of bromine on citraconic acid in a neutral or alkaline solution. The behaviour of the pyrocitric acids with the haloid acids has already been described (p. 935). When heated with a concentrated solution of potassic sulphite, they all form the same sulphosalt, $C_3H_5(COOK)_2(SO_3K)$ (Wieland, *Ann. Chem. Pharm.*, clvii. 34). Concentrated solutions of potassic citra- and mesaconate yield ordinary allylene (methylacetylene) $CH_3.C\equiv CH$, on electrolysis; potassic itaconate, however, furnishes an isomeric hydrocarbon (*allene*), which probably has the formula $CH_2=C=CH_2$, as it is incapable of forming metallic derivatives (Aarland, *Jour. pr. Chem.* [2], vi. 256; vii. 142).

When citraconic acid is heated with nitric acid (sp. gr. 1·45), a violent reaction takes place, and a small quantity of an oily product is obtained, consisting of two substances which may be separated by crystallization from alcohol. The more soluble—the *eulyte* of Baup—crystallizes from chloroform in large, very perfect prisms, melting at 99°·5 (211°·1 F.); it has the formula $C_6H_6N_4O_7$. The second body, Baup's *dyslyte*, crystallizes from boiling alcohol in fine needles, melting at 189° (372°·2 F.); its composition is represented by the formula $C_8H_6N_4O_6$. Both are decomposed by potassic hydrate with formation of brown resinous products (Bassett, *Chem. Soc. Jour.*, 1872, xxv. 98).

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* It would appear that in all cases citraconic acid enters into reaction with other bodies much more readily than either mesa- or itaconic acid.

The pyrocitric acids furnish a number of well-crystallized salts. They differ considerably in their behaviour with ferric chloride, a neutral solution of mesaconic acid behaving exactly like a neutral succinate (comp. Aarland). The ethereal salts require examination.

The constitution of the pyrocitric acids will be discussed later on (p. 985).

(1899) CROTACONIC ACID, isomeric with the pyrocitric acids, is prepared from chlorocrotonic acid (m.p. 97°·5 C.), by acting on the ethylic salt of this acid with potassic cyanide, and treating the resulting potassic cyanocrotonate with hydrochloric acid. It is a crystalline body, melting at 119° (246°·2 F.), which is distinguished from the isomeric acids by the readiness with which it is decomposed with evolution of carbonic anhydride; this decomposition commences at about 130°—135° (266°—275° F.), and takes place rapidly at 140° (284° F.), at which temperature neither citra- nor mesaconic acid yields any gas (Claus, *Ann. Chem. Pharm.* cxci. 68). This behaviour points to the formula $CH_3.CH{=}C(COOH)_2$, and consequently, if crotaconic acid is formed by the mere displacement of the chlorine in the chlorotonic acid by carboxyl, the latter acid should be represented by the formula $CH_3.CH{=}CCl.COOH$. But if this latter be adopted, it is difficult to account for the production of tricarballylic acid (1880) from the chlorocrotonic acid in question, and on the whole the formula $CH_2Cl.CH{=}CH.COOH$ would appear to be the most probable for this acid. The production of crotaconic acid must then be regarded as the final result of a series of changes analogous, perhaps, to those occurring in the formation of crotonic acid from allylic iodide (comp. Pinner, *Deut. chem. Ges. Ber.*, xii. 2053).

(1900) HALOID AND HYDROXY-DERIVATIVES OF MALEIC, FUMARIC AND THE PYROCITRIC ACIDS.—The following are known:

Bromo-derivatives of Maleic and Fumaric Acids.—The recent researches of Fittig and Petri appear to show that only two acids of the formula $C_2HBr(COOH)_2$ exist, and not four as has been supposed; their formation has already been described (1855).

Bromomaleic acid crystallizes from water in large well-formed transparent prisms, melting at 128° (262°·4 F.). On distillation it is decomposed into water and bromomaleic anhydride; when boiled with a dilute solution of hydrobromic acid it undergoes isomeric change, being converted into bromofumaric acid; on treatment with a saturated solution of hydrobromic acid at the ordinary temperature, it readily combines with it; it also unites with it at ordinary temperatures, so that in all respects its behaviour is analogous with that of maleic acid.

Bromofumaric acid (Kekulé's isobromomaleic acid) crystallizes from water in large thick plates, melting at 178° (352°·4 F.). It also is converted into bromomaleic anhydride on distillation; but it is only slowly converted into a dibromosuccinic acid on treatment with a cold saturated solution of hydrobromic acid, and it also unites much more slowly than the isomeric acid with bromine, thus resembling fumaric acid.

Both acids furnish fumaric acid free from maleic acid on reduction, and the conversion of the one acid into the other may be effected through the anhydride, since the latter combines with water to form bromomaleic acid.

On treatment of the chloride of the formula $C_2HCl(COCl)_2$ obtained from tartaric acid (p. 943) with water, an acid is formed which has hitherto been regarded as *chloromaleic acid*, $C_2HCl(COOH)_2$ (Perkin and Duppa), but there is no proof that this is not chlorofumaric acid.

An acid of the formula $C_2Br_2(COOH)_2$ is one of the products of the action of bromine and water on succinic acid (comp. Fittig and Petri).

Chlorocitraconic acid can only exist in aqueous solution. *Chlorocitraconic anhydride*, $C_5H_3ClO_3$, is formed on distilling chlorocitramalic acid (1872); it crystallizes in large plates, melting at 100° (212° F.), but it volatilizes completely at much lower temperatures; it dissolves very slowly in cold water (Swarts, *Bull. Acad. Belg.*, 1872, xxxiii. 31; Gottlieb, *Jour. pr. Chem.* [2], viii. 73.).

Bromocitraconic anhydride, $C_5H_3BrO_3$, is obtained by the action of bromine on pyrotartaric acid; also on distilling dibromocitrapyrotartaric acid (p. 935), and on treating citraconic anhydride with a single molecular proportion of bromine. It is said that a dibromo-derivative may also be prepared by this latter method (Cahours). Bromocitraconic anhydride dissolves in water, forming the corresponding acid, but it may be crystallized from boiling water, so unstable is the acid, separating either as an oil which soon solidifies, or in glistening plates melting at 98° (208°·4 F.). Bromocitraconates may be prepared from the aqueous solution in the ordinary manner (Kekulé, Cahours, Lagermarck, *Zeits. Chem.* [2], vi. 299).

Chloritaconic acid, $C_5H_5ClO_4$, is formed when aconic acid, $C_5H_4O_4$, is heated with fuming hydrochloric acid; it is a crystalline body, but slightly soluble in cold water, and when heated with water readily splits up into aconic and hydrochloric acids. *Bromitaconic acid*, $C_5H_5BrO_4$, is formed in a similar manner, or by heating itadibromopyrotartaric acid alone or with water, and behaves similarly (Swarts, *Bull. Acad. Belg.*, 1872, xxxiii. 31).

Hydroxymaleic acid, $C_4H_4O_5 = C_2H(OH)(COOH)_2$.—According to Bourgoin (*Compt. Rend.*, lxxvi. 1265), this acid is produced on boiling a solution of argentic bromomalate; it crystallizes in long slender needles, easily soluble in water and alcohol.

Dihydroxyfumaric acid, $C_4H_4O_6 = C_2(OH)_2(COOH)_2$, is formed when fumaric acid is oxidised by means of potassium permanganate. It is a white crystalline body less soluble in water than oxalic acid (Tanatar, *Deut. chem. Ges. Ber.*, xii. 2293, and xiii. 159).

Hydroxycitraconic acid, $C_5H_6O_5 = C_3H_3(OH)(COOH)_2$.—Chlorocitraconic acid does not exchange its chlorine for hydroxyl when boiled with a solution of baric hydrate, but hydroxycitraconic acid may be obtained by withdrawing the elements of a molecule of hydrochloric acid from chlorocitramalic acid by boiling its baric salt, either with water alone or, which is better, with a solution of baric hydrate. It crystallizes in large prisms, very soluble in water; when heated for some time at 120° (248° F.) it is converted into a white spongy mass, which slowly dissolves in water, forming citratartaric acid (1871); this latter is also formed on heating the acid or its baric salt with water at 120° (248° F.). Hydroxycitraconic acid very readily combines with hydrochloric acid, forming the acid of the formula $C_3H_3Cl(COOH)_2$; this latter crystallizes in glistening rhombic plates, melting at 161° (321°·8 F.); it is reconverted into the parent acid by heating its baric salt with a solution of baric hydrate; on dry distillation, it is resolved into propionic acid, carbonic oxide, carbonic anhydride, and hydrochloric acid gases, thus differing entirely from the isomeric chlorocitramalic acid (Morawski, *Jour. pr. Chem.* [2], x. 68; xi. 430).

Hydroxyitaconic acid, isomeric with hydroxycitraconic acid, is obtained in a similar manner from chloritamalic acid, and by the addition of the elements of a molecule of water to aconic acid (q.v.); it does not crystallize (Gottlieb, *Jour.*

pr. Chem. [2], xi. 450). No haloid- or hydroxy-derivatives of mesaconic acid are known.

(1901) ACIDS OF THE FORMULA $C_6H_8O_4$.—The only acid of this formula at present known is *hydromuconic acid*, obtained by the action of nascent hydrogen on chloromuconic acid (1878). It forms long needles, melting at 195° (383° F.) (Limpricht).

As pointed out on pp. 885, 887, sodic *a*-hydroxypropionate is decomposed by heating, with loss of the elements of a molecule of water, the residue consisting of sodic acrylate and of a sodic salt of the same empirical composition as this latter, which, when brought into contact with water, combines with it, forming a so-called paradipimalate. Wislicenus regards this sodic salt as derived from a *diacrylic acid*, $C_6H_8O_4$, which, however, cannot be isolated (*Ann. Chem. Pharm.*, clxxiv. 285).

(1902) DEHYDRO-ACIDS RELATED TO ITACONIC ACID.—In this category are included aconic, paraconic and hydroxyparaconic acid, which are monobasic acids formed by the withdrawal of the elements of a molecule of water from hydroxyitaconic, itamalic and itatartaric acid (1871) respectively; muconic acid, homologous with aconic acid, may also be described here.

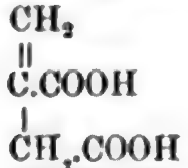
Aconic acid, $C_5H_4O_4$, is best prepared by neutralizing a solution of itadibromopyrotartaric acid with sodic carbonate, then boiling it, and again neutralizing it from time to time with the carbonate until one and a half molecular proportions of the latter has been employed; the sodic aconate, which crystallizes from the solution on cooling in thin plates, is then decomposed by dilute sulphuric acid and the acid extracted with ether.

Aconic acid crystallizes from water, in which it is very soluble, in transparent rhombic prisms, melting at 164° (327°·2 F.); it carbonizes when heated at a higher temperature. Its salts, which are represented by the general formula $C_5H_3O_4M'$, are obtained by neutralizing the aqueous solution of the acid with metallic carbonates, and with the exception of the silver salt are easily soluble in water; metallic hydrates cannot be employed in their preparation, as they at once give rise to the production of hydroxyitaconates. By boiling aconic acid with an excess of baric hydrate, the oxyitaconate first produced is in great part resolved into a mixture of formate and succinate (comp. Meilly, *ibid.*, clxxi. 155).

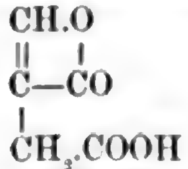
Paraconic acid, $C_5H_6O_4$.—To prepare this acid, a solution of itachloropyrotartaric acid is boiled with argentic carbonate, and the argentic paraconate, $C_5H_5AgO_4$, which crystallizes in needles as the liquid cools, is decomposed with hydric sulphide. It is crystalline, but very soluble in water. The paraconates may be obtained by decomposing a cold solution of the silver salt with metallic chlorides; by heating their solutions, they are converted into acid itamalates (Swarts).

Hydroxyparaconic acid, $C_5H_6O_5$.—The calcic salt of this acid is formed on boiling an aqueous solution of chloritamalic acid (Morawski, *Jour. pr. Chem.* [2], xi. 450).

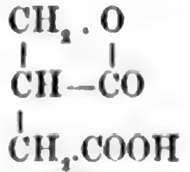
The relation of these three acids to each other and to itaconic acid is indicated by the following formulæ:



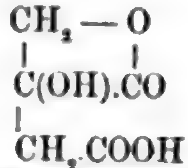
Itaconic acid.



Aconic acid.

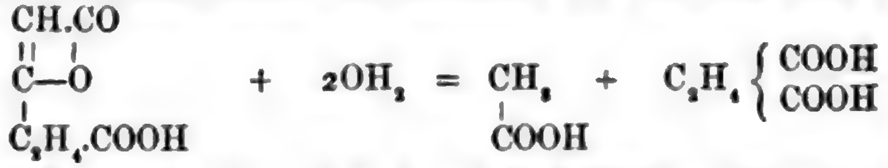


Paraconic acid.



Hydroxyparaconic acid.

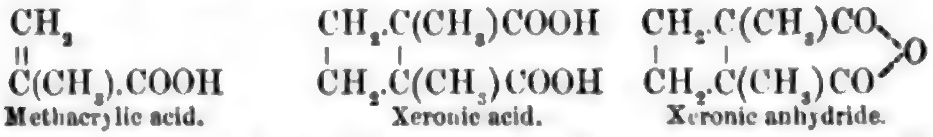
Muconic acid, $C_6H_6O_4$, is formed on adding argentic oxide to a hot aqueous solution of dibromadipic acid from hydromuconic acid (1855) as long as the brown-black colour of the former disappears, then removing the dissolved silver by means of hydrochloric acid or hydric sulphide, and concentrating the filtered solution on the water bath; it crystallizes in large monoclinic prisms, easily soluble in water. When boiled with an excess of a solution of baric hydrate, it is resolved into acetic and succinic acid (Limpricht and Delbruck, *ibid.*, clxv. 274):



$$\begin{matrix}CH.CO\\ \|\quad|\\ C{-}O\\ |\\ C_2H_4.COOH\end{matrix} + 2OH_2 = \begin{matrix}CH_3\\ |\\ COOH\end{matrix} + C_2H_4\begin{cases}COOH\\ COOH\end{cases}$$

(1903) **XERONIC ACID**: $C_8H_{12}O_4 = C_6H_{10}(COOH)_2$.—Citraconic anhydride begins to decompose at about 150° (302° F.) with evolution of carbonic anhydride; when it is distilled, the greater part passes over at about 214° (417°·2 F.), but the thermometer then rises gradually to 250° (482° F.), and an oil distils over which is a mixture of citraconic and xeronic anhydrides. If it is boiled for about two hours in a vessel attached to a reversed condenser, it is converted into a brown viscid syrup, and on submitting this to distillation about one-fourth is obtained boiling at 213°—220° (415°·4—428° F.), after which the thermometer gradually rises to 280° (536° F.), a brown-yellow oil passing over; much of this is volatile in a current of steam, but a portion remains as a brown viscid mass insoluble in ammonia. Citraconic anhydride mixed with only one-sixth of its volume of water does not decompose when similarly treated.

On distilling the mixture of xeronic and citraconic anhydrides with steam, the former passes over as a heavy oil only slightly soluble in water; in the pure state, it boils constantly at 242° (467°·6 F.), and remains liquid even at —18° (0°·4 F.). The acid itself does not appear capable of existing, although its salts are readily obtained. The anhydride dissolves only very slowly in a cold solution of sodic carbonate, although readily soluble in a hot solution; if the liquid is supersaturated with hydrochloric acid, it is at first perfectly clear, but soon becomes turbid from the separation of the anhydride. If the anhydride is digested at a gentle heat with water and calcic carbonate, and the filtered solution is then boiled, *calcic xeronate*, $C_8H_{10}O_4Ca + OH_2$, is deposited as a flocculent precipitate which soon becomes dense and crystalline. The baric salt is obtained in a similar manner. Xeronic anhydride does not combine either with nascent hydrogen or bromine, and as xeronic acid is polymeric with methacrylic acid (p. 958),* and this latter acid or its derivatives are, under certain circumstances, readily obtained from citraconic acid, it appears probable that the two acids are related in the manner indicated by the following formulæ (Fittig, *Ann. Chem. Pharm.*, clxxxviii. 59):



$$\begin{matrix}CH_2\\ \|\\ C(CH_3).COOH\end{matrix} \qquad \begin{matrix}CH_2.C(CH_3)COOH\\ |\qquad|\\ CH_2.C(CH_3)COOH\end{matrix} \qquad \begin{matrix}CH_2.C(CH_3)CO\\ |\qquad|\\ CH_2.C(CH_3)CO\end{matrix}\!\!>\!O$$

Methacrylic acid. Xeronic acid. Xeronic anhydride.

Hexydrophthalic acid, the isomeride of xeronic acid, will be referred to under phthalic acid.

(1904) CAMPHORIC ACIDS: $C_{10}H_{16}O_4 = C_8H_{14}(COOH)_2$.—A number of modifications of camphoric acid have been obtained which do not appear to differ in so-called chemical properties; like the tartaric acids, they are distinguished, however, by their behaviour in polarized light and other differences in their physical properties.

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* The polymerization of methacrylic acid referred to on p. 958, is readily effected by heating the acid in closed tubes at 130° (266° F.). It is completely converted into a white porcelain-like mass, which swells up in water, but without dissolving. This product is scarcely affected by any of the ordinary reagents (Fittig, *Deut. chem. Ges. Ber.*, xii. 1739; *Ann. Chem. Pharm.*, cc. 70).

Dextrocamphoric or *ordinary camphoric acid* is formed by the oxidation of ordinary camphor with nitric acid. It is obtained without difficulty by heating the camphor with nitric acid of about 1·3 sp. gr. for several days on the water-bath, the operation being best performed in a large flask having a tube 3—4 ft. long to act as condenser fitted to its neck. When the oxidation is at an end, as shown by the evolution of red fumes ceasing almost entirely, the liquid is drained from the solid mass of acid and unoxidized camphor, and the latter either digested with a solution of sodic carbonate, or submitted to steam distillation, in order to separate the camphoric acid from the camphor; a considerable quantity of camphoric acid is also obtained on evaporating the nitric acid solution.

Camphoric acid is sparingly soluble in cold, but moderately in hot water, and easily soluble in alcohol. It crystallizes from water in hard semi-transparent prismatic crystals, melting, it is ordinarily said, at about 176° (348°·8 F.); according to Kachler (*Ann. Chem. Pharm.*, cxcvii. 92), the acid purified by conversion first into the soluble baric salt and then into the insoluble cupric salt, and repeated recrystallization from water, crystallizes from alcohol in large transparent monoclinic prisms melting at 178° C. (corr. 180°·7 C.). Riban, however, states that the corrected melting-point is 187° (368°·6 F.), and Armstrong finds 184° C. (uncorr.).

In an aqueous solution, or in acetic acid solutions containing from 3 to 12 grams per 100 c.c., it has the apparent sp. rot. power $[a]_D = 46°$; but its apparent sp. rot. power in alcoholic solutions containing from 2·5 to 19 grams per 100 c.c. is $[a]_D = 47°·5$ (Landolt).

Camphoric acid readily dissolves in concentrated sulphuric acid; on the addition of water, camphoric anhydride, $C_{10}H_{14}O_3$, is precipitated. If the sulphuric acid solution is heated at about 60° (140° F.), pure carbonic oxide is evolved and so-called sulphocamphoric acid, a dibasic acid of the formula $C_{10}H_{16}SO_6$, is produced (comp. Kachler, *ibid.*, clxix. 178). By fusing camphoric acid with potassic hydrate, pimelic acid (1849) is obtained; if distilled with calcic hydrate, it yields phorone (1684). When heated with bromine, it forms a dibromide, $C_{10}H_{16}Br_2O_4$, which crystallizes in ruby-red prisms, but is so unstable that it decomposes on mere exposure to the air into bromine and camphoric acid (Wreden, *ibid.*, clxiii. 330). By heating camphoric acid with a large excess of very concentrated hydriodic acid at 200°—280° (392°—536° F.), it is decomposed into hexhydrometaxylene, $C_6H_{10}(CH_3)_2$, and carbonic anhydride; tetrahydrometaxylene, C_8H_{14}, is also produced when a less concentrated acid is employed. A hydrocarbon isomeric with hexhydrometaxylene is formed in small quantity on dry distillation of cupric camphorate (Wreden, *ibid.*, clxxxvii. 156).

Lævocamphoric acid, formed by oxidation of the lævorotatory camphor from oil of feverfew (*Matricaria partherium*), is said to resemble dextrocamphoric acid in all respects excepting that it has the pôwer of rotating the polarized ray in an opposite direction, but to a precisely equal extent (Chautard).

Paracamphoric acid.—On mixing together concentrated alcoholic solutions of lævo- and dextrocamphoric acid, considerable heat is developed, an abundant precipitate of optically inactive paracamphoric acid being produced. The same acid is obtained by oxidation of the inactive camphor of oil of lavender. By heating this acid with a mixture of alcohol and sulphuric acid, the corresponding ethylic salt is obtained, but on saponification this yields an acid which differs considerably from that employed in its preparation, being almost insoluble in all ordinary media (Chautard, *Compt. Rend.*, lvi. 698).

Mesocamphoric acid.—On heating dextrocamphoric acid for a considerable time with hydriodic acid of sp. gr. 1·6 at about 160° (320° F.), or with very concentrated hydrochloric acid at about 140° (284° F.), it is converted into the more soluble optically inactive mesocamphoric acid. This acid separates from a hot concentrated aqueous solution as an oil, but crystallizes from a dilute solution in fine needles, melting at 113° (235°·4 F.). It appears to be less readily converted into the anhydride, being precipitated by water unchanged from its solution in cold concentrated sulphuric acid; the anhydride obtained by heating it above its melting-point resembles ordinary camphoric anhydride in crystalline form and melting-point (Wreden, *Ann. Chem. Pharm.*, clxiii. 323).

According to Jungfleisch (*Bull. Soc. Chem.*, 1873, xix. 530), if camphoric acid is heated with water at 180°—220° (356°—428° F.), its rotatory power is almost entirely destroyed, and a mixture of two isomeric acids is produced in proportions varying with the temperature; they are best separated by crystallization from acetic acid. The more soluble acid is probably mesocamphoric acid and the less soluble Chautard's paracamphoric acid; by repeated recrystallization, however, the latter is resolved into two optically active modifications of equal but opposite rotatory power.

Synthetic camphoric acid.—By oxidizing the camphene derived from the monohydrochloride prepared from French oil of turpentine (1268) with chromic acid, a camphor is produced which, like natural camphor, is optically active but lævorotatory ($[\alpha]_D = -13°·6$); on oxidizing this camphor with nitric acid, a lævorotatory camphoric acid ($[\alpha]_D = -6·5$) is obtained, which, however, melts at 197° (386°·6 F.) (Riban, *Ann. Chem. Phys.* [5], vi. 387). By treating the optically inactive camphene formed by the action of sulphuric acid on the terpenes, an inactive camphoric acid melting at about 202° (395°·6 F.) is produced (Armstrong and Tilden, *Jour. Chem. Soc. Trans.*, 1879, p. 757). Dextrocamphene from the monohydrochloride from American turpentine yields a dextrorotatory camphoric acid having similar properties, which apparently is also produced on directly oxidizing the monohydrochloride prepared from American turpentine with nitric acid (Armstrong).

(1905) CAMPHORIC ANHYDRIDE, $C_{10}H_{14}O_3$.—This body is obtained with the greatest facility by merely distilling camphoric acid, or by dissolving it in sulphuric acid and precipitating with water; it crystallizes from alcohol in glistening prisms melting at 217° (422·6 F.), and boils above 270° (518° F.) without undergoing decomposition. It is converted into the acid only by prolonged boiling with water, in which it is slightly soluble; but it readily dissolves in alkalies, at once undergoing hydration. On treatment with phosphoric pentachloride, it yields camphoric chloride, $C_8H_{14}(COCl)_2$, as an oily liquid which decomposes on distillation. When triturated with baric peroxide and water, it furnishes a solution having powerful oxidizing properties, which Brodie ascribes to the presence of a compound of camphoric peroxide with baric oxide.

The anhydride obtained from synthetical camphoric acid has a higher melting-point (234° C.) than that from ordinary camphoric acid.

Camphoric anhydride combines with bromine, forming a dibromide which decomposes into bromine and the anhydride on mere exposure to the air; but if it is heated with bromine at 110°—130° (230°—266° F.), it is converted into *bromocamphoric anhydride*, $C_{10}H_{13}BrO_3$, a crystalline substance melting at 215° (419° F.). This compound exchanges its bromine for hydroxyl when boiled with water, forming *hydroxycamphoric anhydride*, $C_{10}H_{13}(OH)O_3$. This latter body possesses somewhat remarkable properties. It crystallizes from alcohol, in which it is moderately soluble, in needles melting at 200° (392° F.); but when crystallized from water, it forms hydrated crystals which become anhydrous on exposure over sulphuric acid *in vacuo*. By saturating its solution in anhydrous alcohol with hydrochloric acid, it is converted into the ethylic salt $C_{10}H_{13}(C_2H_5)O_4$, which crystallizes in thin prisms melting at 63° (145°·4 F.). Corresponding metallic salts are readily obtained.

The cadmic salt forms transparent prisms of the composition $(C_{10}H_{13}O_4)_2Cd + 3OH_2$, which are rendered anhydrous by heating at 100° (212° F.).

By heating bromocamphoric anhydride with a concentrated solution of ammonia at 150° (302° F.), it is converted into *amidocamphoric anhydride*, $C_{10}H_{13}(NH_2)O_3$, which crystallizes from alcohol in long needles melting at 208° (406° F.). *Amidocamphoric acid*, $C_8H_{13}(NH_2)(COOH)_2$, is obtained by boiling this compound with a dilute solution of potassic hydrate, &c.; it crystallizes in glistening prisms, and melts at 160° (320° F.), but is at the same time converted into the anhydride and water. Amidocamphoric anhydride and acid are both converted into hydroxycamphoric anhydride when boiled with a concentrated solution of potassic hydrate, or submitted to the action of nitrous acid (Wreden, *Ann. Chem. Pharm.*, clxiii. 330).

(1906) ACIDS FORMED TOGETHER WITH CAMPHORIC ACID BY OXIDATION OF CAMPHOR.*—Although camphoric acid is the chief product, it is not the only acid formed on oxidizing camphor with nitric acid: the mother-liquor remaining after the camphoric acid has been separated as far as possible by crystallization contains, besides a further quantity of this acid and a minute amount of the isomeric mesocamphoric acid, camphoronic acid, $C_9H_{12}O_5$, hydro-oxycamphoronic acid, $C_9H_{14}O_6$, an acid of the formula $C_9H_{12}O_7$, an acid which is probably represented by the formula $C_7H_{12}O_5$, so-called dinitrohephtylic acid, $C_6H_{10}N_2O_6$, and lastly a syrupy acid of unknown formula. The separation of these acids has been described by Kachler (*Ann. Chem. Pharm.*, cxci. 143).

According to Kachler (*Ann. Chem. Pharm.*, clxii. 267), Berthelot's camphic acid, obtained by heating camphor at a high temperature with an alcoholic solution of potassic hydrate, consists of an acid resin and campholic acid, $C_{10}H_{18}O_2$; but Montgolfier (*Ann. Chim. Phys.* [5], xiv. 5) states that it is a mixture of camphic acid, $C_{10}H_{16}O_2$, with phoronic acid, $C_9H_{16}O_2$. The properties assigned to the former are so indefinite, however, that it may be doubted whether such an acid has been separated in a state of purity. According to the latter observer, if dry air is passed through a solution of sodium camphor (*i.e.*, the mixture of sodium camphor and sodium borneol formed on treating camphor with sodium) in boiling crude xylene (b. p. 125°—130° C.), camphic and camphoric acids and a resin are produced; but if a mixture of sodium camphor with a considerable amount of free camphor is heated in sealed tubes at 280° (536° F.), campholic acid is produced. Montgolfier supposes that the formation of campholic acid in this manner is the result of the action of the camphor on the sodium borneol.

Campholic acid, $C_9H_{17}.COOH$, crystallizes in thin prisms melting at 106° (222°·8 F.); it may be distilled unchanged, and is also volatile in a current of steam. Campholic acid has a considerable dextrorotatory power ($[a]_j = 49°·8$). On oxidation with nitric acid, it yields camphoric and camphoronic acids, the former being also produced on heating it with moist bromine. By distilling potassic campholate with soda lime, *campholene*, a hydrocarbon of the formula C_9H_{16} is produced (Kachler).

Camphoronic acid.—According to Kachler, this acid, in the air-dry state, has the formula $C_9H_{14}O_6$, and is not altered by heating at 100° (212° F.); but if it be fused, or heated at 130° (266° F.), it loses a molecule of water, becoming $C_9H_{12}O_5$. The anhydrous acid melts at 115° (239° F.), and the hydrated acid at about 110° (230° F.). According to Kissling (*Inaug. Diss. Tübingen*, 1878), the body $C_9H_{14}O_6$ is the true acid; but this loses a molecule of water on heating at about 80° (176° F.), and is converted into the dehydro-acid $C_9H_{12}O_5$, which melts at 137° (278°·6 F.); the latter volatilizes to an appreciable extent even at 80° (176° F.).

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* Ballo has recently shown (*Deut. chem. Ges. Ber.*, xii. 1597) that, although camphor is not oxidized by heating at 100° (212° F.) with a solution of potassic dichromate and sulphuric acid (comp. 1687), it undergoes oxidation if the solution be boiled; the products are the same as when nitric acid is employed (Kachler, *ibid.*, xiii. 1487).

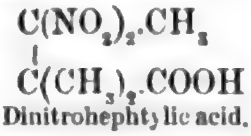
Camphoronic acid forms white microscopic needles, extremely soluble in water, alcohol, and ether. Its most characteristic salt is the baric salt, which is precipitated on boiling an ammoniacal solution of the acid with baric chloride. This salt, according to Kachler, has the formula $C_9H_9Ba_3O_6 + OH_2$, being deprived of a molecule of water by heating at 165° (329° F.). By digesting an alcoholic solution of the acid with sulphuric acid, a diethylic salt of the formula $C\ H_{12}O_6(C_2H_5)_2$ is produced; this salt, however, partially decomposes on distillation into alcohol and a monethylic salt of the formula $C_9H_{11}(C_2H_5)O_5$ is derived from the dehydro-acid, $C_9H_{12}O_5$; this monethylic salt is also obtained on submitting the diethylic salt to the action of acid chlorides (Kissling). Camphoronic acid is not affected by nascent hydrogen, but on fusion with potassic hydrate it yields butyric acid (Kachler), being decomposed in accordance with the equation $C_9H_{12}O_5 + H_2 + H_2O = 2C_4H_8O_2 + CO_2$; according to Kissling, however, acetic and *iso*butyric acids are produced.

The acid $C_9H_{12}O_5$ is not altered by bromine even at 135° (275° F.), but the hydrated acid $C_9H_{14}O_6$ is converted by its action into *oxycamphoronic acid*, $C_9H_{12}O_6$. This acid crystallizes in large prisms of the composition $C_9H_{12}O_6 + OH_2$, which become anhydrous at 100° (212° F.); the anhydrous substance melts at 210° (410° F.), and may be distilled unchanged. It does not appear to be capable of exchanging more than two atoms of hydrogen for metals (Kachler). According to Montgolfier (*loc. cit.*), camphoronic acid is optically active ($[\alpha]_D = -18° 42'$).

Hydro-oxycamphoronic acid: $C_9H_{14}O_6$.—This acid crystallizes from water in large triclinic prisms, melting at 164°·5 (328°·1 F.); it is moderately soluble in cold and very easily soluble in hot water. Hydro-oxycamphoronic acid appears to be tribasic, as it exchanges three atoms of hydrogen for the equivalent amount of metal on treatment with metallic carbonates. When heated with bromine, it is converted into a new acid, melting at 226° (438°·8 F.); this probably has the formula $C_9H_{12}O_6$.

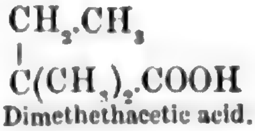
Phoronic acid, $C_9H_{16}O_2$, is almost insoluble even in boiling water, but very soluble in alcohol, from which it crystallizes in thick plates, melting at 169° (336°·2 F.); at a higher temperature it appears to distil unchanged. It has a considerable dextrorotatory power ($[\alpha]_D = +23°$). The metallic phoronates are mostly insoluble in water, but soluble in alcohol (Montgolfier).

Dinitrohephtylic acid: $C_6H_{10}N_2O_6$.—This acid, discovered by Kullhem (*Ann. Chem. Pharm.*, clxiii. 231), has been further investigated by Kachler (*ibid.*, cxci. 155). It is slightly soluble in cold, more easily soluble in hot water, crystallizing from the latter in white laminæ, which are seen under the microscope to consist of rhombic plates. It melts at 215° (419° F.), and may be volatilized unchanged if very carefully heated, but if quickly heated it decomposes with detonation. Dinitrohephtylic acid acts as a monobasic acid, yielding a number of well crystallized salts. By the action of sodium amalgam on its alcoholic solution, mononitrohephtylic acid, $C_6H_{11}NO_4$, is produced, half the nitrogen being eliminated as ammonia; this latter compound exhibits the behaviour of the so-called pseudonitrols (1204). By the action of tin and hydrochloric acid, dinitrohephtylic acid is decomposed with formation of methylisopropylketone, $CH_3.CO.CH(CH_3)_2$, hydroxylamine, ammonia and carbonic anhydride; alkalies act upon it in a similar manner. Mononitrohephtylic acid yields methylisopropylketone and hydroxylamine when decomposed by nascent hydrogen. From these reactions, it appears probable that dinitrohephtylic is a derivative of dimethethacetic acid (Kachler):



$$\begin{array}{l} C(NO_2)_2.CH_3 \\ | \\ C(CH_3)_2.COOH \end{array}$$

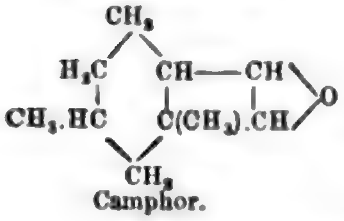
Dinitrohephtylic acid.



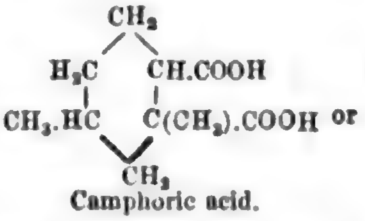
$$\begin{array}{l} CH_2.CH_3 \\ | \\ C(CH_3)_2.COOH \end{array}$$

Dimethethacetic acid.

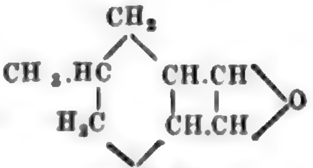
(1907) CONSTITUTION OF CAMPHORIC ACID.—It has already been pointed out under camphor (p. 792) that the formulæ which have been proposed for this acid do not satisfactorily express its general behaviour. The readiness with which it is converted into the anhydride necessitates the assumption that the carboxyl groups are associated with contiguous carbon atoms as in phthalic acid (q. v.); its conversion into hexhydrometaxylene when heated with hydriodic acid (Wreden) renders it highly probable that it is a derivative of this hydrocarbon. The most probable formulæ for camphor and camphoric acid, when these facts are considered, would appear to be the following (comp. Armstrong, *Deut. chem. Ges. Ber.*, xi. 1698):



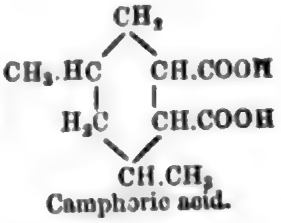
Camphor.



Camphoric acid.

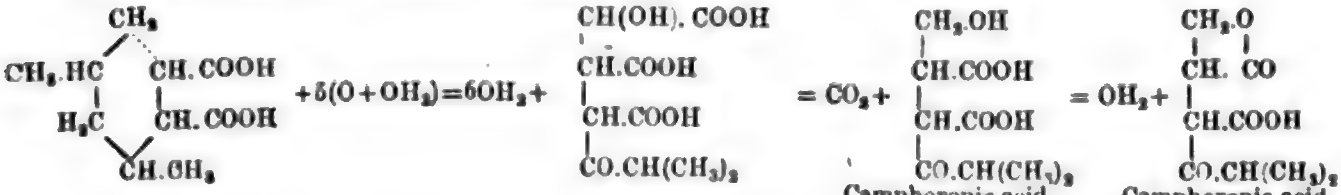


Camphor.



Camphoric acid.

On the supposition that camphoric acid is represented by the second of these formulæ, the formation of a body with the properties of camphoronic acid may be supposed to take place in the following manner, the dotted line indicating the point at which the "chain" becomes broken:



Camphoronic acid (Kissling[*]). Camphoronic acid. (Kachler)

The formation of so-called dinitrohephtylic acid may also be expressed with the aid of the same formula if it be supposed that this acid has the formula $CH_2(COOH).C(NO_2)_2.CH(CH_3)_2$, which differs but slightly from that proposed by Kachler, and equally well represents his results. The assumption that camphoronic acid contains a Ketonic group is not, however, alogether in acccord with its properties.

The corresponding formula for camphor, it will be said, does not directly account for the formation of cymene or normal-propylmethylbenzene; but there can scarcely be a doubt that the production of this hydrocarbon involves a profound isomeric change, and admitting even that camphor contains the C_3H_7 group, as has been supposed, the whole of the evidence we possess goes to show that it must contain *iso* and not *normal* propyl.

§ VIII. ACIDS OF THE $C_nH_{2n-3}(COOH)_3$ SERIES.

(1908) ACONITIC ACID: $CH(COOH)=C(COOH).CH_2(COOH) = C_6H_6O_6$.—This acid is the only member of the series at present known. It was originally discovered in *Aconitum napellus,* but has also been obtained from other species of *Aconitum,* from *Delphinium consolida,* and a number of species of *Equisetum;* from the juice of the sugar-cane (Behr), &c. It may be prepared from citric acid, either by heating it alone (comp. Pawolleck, *Ann. Chem. Pharm.,* clxxviii. 150), or by passing a current of hydrochloric acid gas through citric acid heated at 140° (284° F.) (Hunäus, *Deut. chem. Ges. Ber.,* ix. 1751).

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[*] Kissling represents camphoronic acid by the slightly different formula $CH(OH)(COOH).CH_2.CO.CH(COOH).CH(CH_3)_2$. He doubts whether it can be formed by the further oxidation of camphoric acid.

Aconitic acid is very soluble in water, from which it crystallizes in groups of small white needles; it melts at about 188° (370°·4 F.), but it is difficult to determine the exact point, as in melting it partially decomposes into itaconic acid and carbonic anhydride (Behr, *ibid.,* ix. 351). On treatment with nascent hydrogen, it yields tricarballylic acid. But few of its salts crystallize well.

By heating citric acid in sealed tubes with concentrated hydrochloric acid at 170° (338° F.) Geuther and Hergt (*Jour. pr. Chem.* [2], viii. 372) have obtained a dibasic acid of the formula $C_9H_{12}O_6$, which they term *diconic acid;* this acid is also formed by treating aconitic acid in a similar manner.

Under the name of *aceconitic acid,* Baeyer has described an acid obtained by the action of sodium on ethylic bromacetate, which is apparently isomeric with aconitic acid (*Ann. Chem. Pharm.,* cxxxv. 306).

§ IX. ACIDS OF THE C_nH_{2n-3}.COOH SERIES.

(1909). This series includes tetrahydrobenzoic acid, diallylacetic acid, and the following homologous acids derived from hydrocarbons of the acetylene series:*

Tetrolic acid	C_3H_3.COOH
Sorbic acid	C_5H_7.COOH
Palmitolic acid	$C_{15}H_{27}$.COOH
Stearolic acid	$C_{17}H_{31}$.COOH
Behenolic acid	$C_{21}H_{39}$ COOH

(1910) TETROLIC ACID, *Methacetylenecarboxylic acid*: $C_4H_4O_2 = CH_3.C{\equiv}C.COOH$, was originally prepared by Geuther by decomposing ethylic *a*-chlorocrotonate (1894) by warming it with only a slight excess of potassic hydrate and a little alcohol, &c. (*Jour. pr. Chem.* [2], iii. 448). It has since been obtained by the action of carbonic anhydride gas on sodium allylene,†

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* Chloro and bromopropiolic acids (1893) are derivatives of acetylenecarboxylic acid, HC≡C.COOH, the first term of the series.

† Sodium allylene is obtained by the action of sodium on an ethereal solution of allylene. When isopropacetylene is treated with sodium, it appears to yield

$CH_3.C{\equiv}CNa$ (Lagermark, *Deut. chem. Ges. Ber.*, xii. 853). Tetrolic acid crystallizes from water, in which it is very soluble, in transparent rhombic plates, melting at 76°·5 (167°·7 F.); according to Geuther, it boils without decomposition at 203° (397°·4 F.), but, according to Lagermark, it partially decomposes and is completely resolved into allylene and carbonic anhydride at about 210° (410° F.). It is readily decomposed when heated with potassic hydrate solution, but yields volatile products; probably acetone and potassic carbonate are formed (comp. Kahlbaum, *ibid.*, xii. 2337).

(1911) **Sorbic Acid**: $C_6H_8O_2 = C_5H_7.COOH$.—This acid is a constituent of the unripe berries of the mountain ash (*Sorbus aucuparia*). It crystallizes in long needles, melting at 134°·5 (274°·1 F.), almost insoluble in cold, but moderately soluble in hot water. Sorbic acid readily volatilizes in a current of steam. On distilling it alone, it commences to boil at about 230° (446° F.), but does not pass over entirely, a portion undergoing conversion into a resinous substance; the odour of acraldehyde is perceptible during the distillation. It very readily combines with two atoms of hydrogen, forming hydrosorbic acid (1889). It also combines easily with bromine, forming either a dibromide (dibromhydrosorbic acid), $C_6H_8Br_2O_2$, or a tetrabromide (tetrabromocaproic acid), $C_6H_8Br_4O_2$, according to the proportions employed; these compounds both crystallize well. The tetrabromide is reconverted into sorbic acid by the action of nascent hydrogen. Sorbic acid is less readily acted upon by potassic hydrate than hydrosorbic acid, and when fused with it does not appear to furnish any characteristic product (comp. Fittig and Barringer, *Ann. Chem. Pharm.*, clxi. 307; Fittig and Kachel, *ibid.*, clxviii. 276, cc. 55).

(1912) **Diallylacetic Acid**: $C_8H_{12}O_2 = CH(C_3H_5)_2.COOH$.—This acid is obtained by the action of alkalies on ethylic acetodiallylacetate (p. 912). It is a colourless liquid, boiling at 224° (435°·2 F.) (Reboul, *Compt. Rend.*, lxxxiv. 1233; Wolff, *Deut. chem. Ges. Ber.*, x. 1956).

(1913) **Palmitolic acid**, $C_{16}H_{28}O_2 = C_{15}H_{27}.COOH$, prepared from the dibromo-acid obtained by combining either hypogæic or gaïdic acid (1890) with bromine by heating it with an alcoholic solution of potassic hydrate, &c., crystallizes in fine silky needles, melting at 42° (107°·6 F.), insoluble in water,

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both sodium isopropacetylene and sodium isopropethylene, as two acids corresponding to these bodies are formed on treating the product with carbonic anhydride (Lagermark).

Demarçay has stated that when ethylic acetomethacetate (1827) is submitted to the action of bromine, and the resulting monobrominated derivative is treated with an alcoholic solution of potassic hydrate, a crystalline acid is obtained to which he assigns the formula $C_{12}H_{14}O_7 = 3C_4H_4O_2 + OH_2$; this acid is said to form remarkable salts, the group C_4H_4O acting like SiO_2, *e.g.*, several such groups uniting with one or more molecules of baric oxide. Homologous acids are formed in a similar manner from the homologues of ethylic acetomethacetate, and by acting on the dibrominated derivatives of the homologues of ethylic acetoacetate, corresponding hydroxy-acids are produced. These acids are termed *tetric, pentic, oxytetric*, &c., by Demarçay (*Compt. Rend.*, lxxxiv. 1032; lxxxvi. 1085, 1135; lxxxviii. 126, 289; lxxxvii. 351). The formation of acids of such a composition, having such unusual properties, in this manner appears highly remarkable; so much so that their existence must be regarded as problematical.

but very easily soluble in alcohol. It combines with bromine, forming a dibromide, $C_{16}H_{28}Br_2O_2$, and a tetrabromide, $C_{16}H_{28}Br_4O_2$. On oxidation with nitric acid, it yields palmitoxylic acid, $C_{16}H_{28}O_4$, a monobasic acid which crystallizes in plates, melting at 67° (152°·6 F.), together with suberic acid, $C_6H_{12}(COOH)_2$, and a third substance said to be the "aldehyde-acid," $C_8H_{14}O_3$, derived from suberic acid; but judging from the results obtained with stearolic acid (q. v.) the substance supposed to have this composition was probably impure octylic acid (Schröder, *ibid.*, cxliii. 22).

(1914) STEAROLIC ACID, $C_{18}H_{32}O_2 = C_{17}H_{31}\ COOH$.—To prepare this acid, pure oleic acid is combined with bromine, and the resulting dibromide heated in the water-bath with an excess of an alcoholic solution of potassic hydrate, &c. It may also be obtained from elaïdic acid (q. v.) (Overbeck, *ibid.*, cxl. 39). Stearolic acid crystallizes from alcohol in long white prisms, melting at 48° (118°·4 F.); when heated to a temperature of about 260° (500° F.) it distils for the greater part unchanged. If mixed with a single molecule of bromine, it forms the dibromide $C_{18}H_{32}Br_2O_2$, but if exposed with an excess of bromine to sunlight, the tetrabromide, $C_{18}H_{32}Br_2O_2$, is produced. According to Overbeck, it yields stearoxylic acid, $C_{18}H_{32}O_4$, azelaic acid, $C_7H_{14}(COOH)_2$, and the "aldehyde-acid" corresponding with the latter; but according to Limpach, Overbeck's aldehyde-acid is a mixture of normal primary nonylic (pelargonic) acid, $C_8H_{17}.COOH$, with a dinitroso-acid (*ibid*, cxc. 294). Stearoxylic acid crystallizes from alcohol in yellowish glistening plates, melting at 86° (186°·8 F.); it is monobasic.

(1915) BEHENOLIC ACID, $C_{22}H_{40}O_2 = C_{21}H_{39}.COOH$, prepared from the dibromide of erucic acid, crystallizes from alcohol in glistening needles, which melt at 57°·5 (135°·5 F.) Like palmitolic and stearolic acids, it does not combine with nascent hydrogen, but unites with bromine in two proportions, forming a dibromide and a tetrabromide, both crystalline. It also behaves similarly on oxidation with nitric acid, yielding a monobasic acid of the formula $C_{22}H_{40}O_4$, which crystallizes from alcohol in small glistening yellowish plates, melting at about 91° (195°·8 F.), together with brassylic acid, $C_9H_{18}(COOH)_2$, and an oily substance supposed to be the half aldehyde of this latter acid, but which perhaps is impure endecylic acid, $C_{10}H_{21}.COOH$ (Hausknecht, *ibid.*, cxliii. 40).

(1916) TETRAHYDROBENZOIC ACID; *Hydrobenzoic* or *benzoleic acid*, $C_7H_{10}O_2 = C_6H_9.COOH$.—This acid, although having the composition of a member of the $C_nH_{2n-3}.COOH$ series, is not truly homologous with the acids previously described, which undoubtedly are all derivatives of hydrocarbons in the formulæ of which the carbon atoms are represented as forming an open chain; whereas hydrobenzoic acid is derived from the closed chain hydrocarbon C_6H_{10} formed by the union of four atoms of hydrogen with benzene. It is prepared by digesting a hot saturated solution of benzoic acid with sodium amalgam, the solution being maintained acid by adding hydrochloric acid from time to time; the solution of sodic salt thus obtained is then acidulated and the hydrobenzoic acid extracted with ether (Herrmann, *Ann. Chem. Pharm.*, cxxxii. 77). It is also formed together with benzylic alcohol and glycine by the action of hydrating agents on so-called hydrobenzyluric acid, $C_{16}H_{21}NO_3$, the product of the action of nascent hydrogen on hippuric acid (Otto, *ibid.*, cxxxiv. 315). According to Herrmann, it is a mobile colourless liquid, heavier than water, in which it is only slightly soluble, and possesses an extremely unpleasant odour like that of valeric acid; but Otto states that it is a crystalline substance. Both the acid and its salts rapidly undergo oxidation on exposure to the air, benzoic acid or a benzoate being formed, and therefore it is very difficult to obtain them pure.

§ X. ACIDS OF THE $C_nH_{2n-4}(COOH)_2$ SERIES.

(1917) Two acids of this series are known, *acetylenedicarboxylic acid*, $C_2(COOH)_2$, and *tetrahydrophthalic acid* (see phthalic acid), $C_6H_8(COOH)_2$.

(1918) ACETYLENEDICARBOXYLIC ACID: $COOH.C{\equiv}C.COOH = C_4H_2O_4$.—This acid is formed in almost theoretical amount on heating dibromo- or isodibromosuccinic acid (1855) with excess of an alcoholic solution of potassic hydrate; a violent reaction takes place, especially with the latter, and a crystalline precipitate of the potassic salt of the new acid separates out. This is dissolved in water, the solution acidulated with dilute sulphuric acid, extracted with ether, and the ethereal solution is then set aside to crystallize. Acetyleneccarboxylic acid crystallizes with two molecules of water, which it loses on exposure over sulphuric acid. It is extremely soluble in water, alcohol and ether. It decomposes slowly at 100° (212° F.), and very rapidly at about 180° (356° F.). Its salts crystallize well, but are very unstable (Bandrowski, *Deut. chem. Ges. Ber.*, x. 838; xii. 2212).

§ XI. THE VAN'T HOFF-LE BEL HYPOTHESIS OF ISOMERISM.

So many instances of exceptional isomerism have been referred to in describing the foregoing acids, that it appears desirable to discuss these before proceeding further.

(1919) INSUFFICIENCY OF THE PRESENT THEORY OF ISOMERISM.—It is now a well-established fact that compounds exist differing more or less considerably in certain physical properties, but so similar in what is ordinarily termed their general chemical behaviour that they can only be represented in accordance with our present system of symbolic notation by identical formulæ: in other words, our present theory of isomerism is found to be insufficient.

The compounds referred to are, among others, the diphenylglycols (hydrobenzoins), mannitol and dulcitol and the allied carbohydrates of the formula $C_6H_{12}O_6$ as well as mucic and saccharic acids, the lactic acids, the tartaric acids, fumaric and maleic acids, and the two pyrocitric acids, citraconic and mesaconic acids. It will be desirable to briefly point out the exceptional instances of isomerism afforded by these and other compounds before describing the hypothesis advanced by Van't Hoff and Le Bel to explain such cases of isomerism.

Among hydrocarbons, the only example of isomerism which apparently cannot be explained by the existing theory, is that furnished by those of the formula $C_{10}H_{16}$—the *terpenes* and *citrenes*.* The number of distinct terpenes and citrenes probably is much fewer than is commonly supposed, the majority of the natural products being mixtures; but whatever their number and whatever the relation between these two groups of hydrocarbons, there can be no doubt of the existence of at least two terpenes—one dextrorotatory, the other lævorotatory—and of at least two similarly related citrenes. Chemically these isomeric terpenes appear to be in no way distinguishable, and the same is true of the citrenes.

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* Excepting perhaps sylvestrene, all the hydrocarbons of the formula $C_{10}H_{16}$ derived from various essential oils, &c., appear to belong to one or other of two classes: those boiling at about 156° (312°·8 F.), which are conveniently termed *terpenes*, and those boiling at about 178° (352°·4 F.), which may be distinguished as *citrenes*.

Among haloid derivatives of hydrocarbons, no such instances have as yet been met with. A number of crystallinehaloid-nitro-derivatives of benzene have been obtained in two or more forms, differing in crystallographic characters and melting-point: but in the case of the particular compounds referred to, it has been found possible not only to convert the one form into the other by merely bringing the two kinds of crystals into contact, or by adding the crystal of the one form to the liquid resulting from the fusion of the other; but also to effect the reverse change (*i.e.*, to convert the relatively stable into the relatively unstable modification) by suddenly cooling the fused substance (comp. Jungfleisch, *Ann. Chim. Phys.* [4] xv., 186; v. Richter, *Deut. chem. Ges. Ber.* viii. 1427; Laubenheimer, *ibid.*, ix. 766). Such crystalline modifications are probably composed of molecular aggregates of different degrees of complexity;* they are sharply distinguished from isomerides of the character now under discussion by the fact that although it is possible to convert the one isomeride into the other, in some cases, by the mere agency of heat, the reverse change cannot be effected except perhaps by an indirect process involving the combination of the substance with some other body, and the subsequent removal of the elements of this body.

The isomerism of the two diphenylglycols known as hydrobenzoin and isohydrobenzoin has already been discussed (1525). Further experimental evidence of the identity of the two alcohols from a chemical point of view has recently been adduced by Zincke and Breuer (*Ann. Chem. Pharm.* cxcviii., 115), and it would appear to be impossible to represent their behaviour on treatment with various reagents, except by the employment of the same formula for both.

Mannitol and dulcitol, being both derivatives of normal hexane and relatively very stable compounds, are necessarily represented by the one formula $CH_2(OH).(CH.OH)_4.CH_2(OH)$ (comp. p. 559). The isomeric carbohydrates —dextrose, lævulose and galactose—which furnish these alcohols on hydrogenation, are, it can now scarcely be doubted, all bodies of the formula $CH_2(OH).(CH.OH)_4.COH$. Saccharic and mucic acids must also be represented by one formula, $COOH.(CH.OH)_4.COOH$, both on account of their relation to mannitol and dulcitol, and of their general chemical behaviour.

Ordinary fermentation lactic acid and the isomeric optically active acid do not differ in any of their reactions, but merely in their optical characters and in the amounts of water of crystallization associated with some of their salts.

Dextro- and lævotartaric acids exhibit the most absolute similarity excepting in their behaviour in polarized light and the position of a certain face on the crystals; and the existing theory appears to be quite incapable of explaining their isomerism. The relation which the third modification, mesotartaric acid, bears to them is also at present entirely matter for speculation; there would appearto be no reason to suppose, however, that it differs from them in molecular weight.

Several modifications of maleic acid corresponding to the several modifications of tartaric acid are known. Camphoric acid in like manner exists in several modifications, corresponding, it would seem, to those of tartaric acid.

The acrylic series affords several exceptional instances, the isomerism of crotonic and isocrotonic acids, of angelic and $\alpha\beta$-dimethacrylic acids, and probably also of oleic and elaïdic acids, being apparently of the character now under discussion.

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* The two crystalline modifications of dibromopropionic acid described by Tollens, and the crystalline modifications of diphenylketone, phenyltolylketone, and of isohydrobenzoin diacetate are also doubtless physical modifications of this kind.

Maleic and fumaric acids, and citraconic and mesaconic acids, are especially interesting examples of exceptional isomerism. Maleic and fumaric acids both furnish ordinary succinic acid when hydrogenized, and they may be distilled without losing the elements of carbon dioxide; we must therefore consider the two carboxyl groups in each acid to be associated with different carbon atoms. But there is only one formula possible on such an assumption, viz., $COOH.CH{=}CH.COOH$; unless, as Fittig has recently suggested (*Ann. Chem. Pharm.*, clxxxviii. 95), it be supposed that in so-called unsaturated compounds carbon atoms having free "affinities" may be present (comp. 1058, 1227); on this assumption, the formula $COOH.CH_2.C.COOH$ is also possible.

Similarly there are only two formulæ by which it is possible to represent the three pyrocitric acids, as they all furnish methylsuccinic acid when hydrogenized; one of these, viz., $CH_2{=}C(COOH).CH_2.COOH$, must be assigned exclusively to itaconic acid; the second, viz., $CH_3.C(COOH){=}CH.COOH$, applies both to citraconic and mesaconic acids; we may, however, as Fittig suggests, represent the one acid by this formula and the other by the formula $CH_3.CH(COOH).C.COOH$.

This hypothesis, although applicable to fumaric and maleic acids, and to the homologous pyrocitric acids, and also to the above-mentioned acids of the acrylic series, does not, however, furnish any "explanation" of the isomerism of saturated compounds such as mannitol and dulcitol, the tartaric acids, &c.

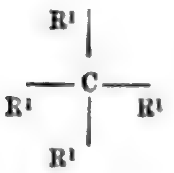
The last case of exceptional isomerism among the acids to which attention may be here drawn is that of the two hexhydromellitic acids (q. v.), both of which are bodies of great stability.

In addition to the before-mentioned instances among compounds in all of which carbon is the grouping element, the isomerism of sulphur diethmethiodide and sulphur ethmethethiodide (p. 710), in which sulphur is the grouping element, may be mentioned as probably an example of the same kind. Among compounds in which nitrogen is the grouping element, the dibenzoylanisyl and dianisylbenzoyl derivatives of hydroxylamine (q. v.) described by Lossen, furnish instances of isomerism which it is difficult, if not impossible, to explain in accordance with the existing theory.

The formulæ at present employed are all constructed on the hypothesis that the several "units of affinity" of a polyad atom such as that of carbon, sulphur, or nitrogen, are of the same value and have identical functions. The number of isomerides possible on this assumption is much fewer than on the hypothesis that the several units of affinity are not all of the same value; but the admission of this latter hypothesis is precluded by the fact that none of the simpler derivatives of methane, &c., exist in a greater number of modifications than is required on the former hypothesis: for if we bear in mind the extent to which the investigation of these simpler derivatives has been carried, it appears highly improbable that some evidence of the existence of this greater number of isomerides would not ere this have been discovered.

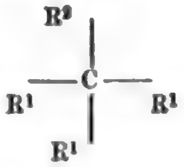
Assuming, however, that graphic formulæ really represent the relative mode of arrangement of the atoms, it may be supposed that even if in a compound such as methane the hydrogen atoms have identical functions, isomeric derivatives are possible, since the radicles introduced in place of the hydrogen atoms may occupy relatively different positions. Thus, although only one compound of the form $C(R^1)_4$ (I.) and one of the form $C(R^1)_3R^2$ (II.) are possible, a compound of the form $C(R^1)_2(R^2)_2$ may exist in two (III. and IV.), and one of the form $CR^1R^2R^3R^4$ in no less than three modifications (V., VI., and VII.); and in the formula $C(R^1)_3R^2$ (VIII.) the radicle $(R^1)^\beta$ has a different value from that of either of the radicles $(R^1)^\alpha$ on account of the difference in its position relatively to R^2, so that in a compound such as chloromethane, for example, one of the hydrogen atoms should have a special value. Conclusions of this kind are so manifestly opposed to all experience that they may at once be dismissed from consideration.

I.



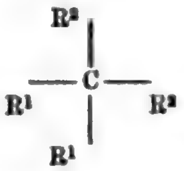
$$\begin{array}{ccc} & R^1 & \\ R^1 & C & R^1 \\ & R^1 & \end{array}$$

II.



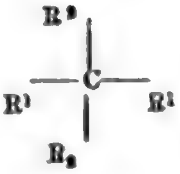
$$\begin{array}{ccc} & R^2 & \\ R^1 & C & R^1 \\ & R^1 & \end{array}$$

III.



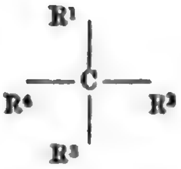
$$\begin{array}{ccc} & R^2 & \\ R^1 & C & R^2 \\ & R^1 & \end{array}$$

IV.



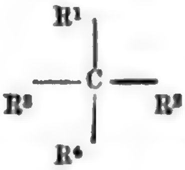
$$\begin{array}{ccc} & R^2 & \\ R^1 & C & R^1 \\ & R_2 & \end{array}$$

V.



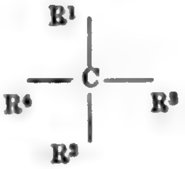
$$\begin{array}{ccc} & R^1 & \\ R^4 & C & R^2 \\ & R^3 & \end{array}$$

VI.



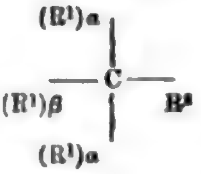
$$\begin{array}{ccc} & R^1 & \\ R^3 & C & R^2 \\ & R^4 & \end{array}$$

VII.



$$\begin{array}{ccc} & R^1 & \\ R^4 & C & R^3 \\ & R^2 & \end{array}$$

VIII.

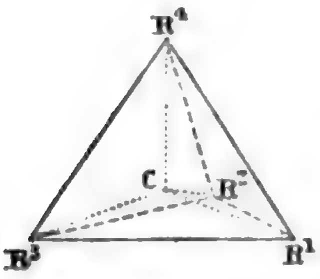


$$\begin{array}{ccc} & (R^1)\alpha & \\ (R^1)\beta & C & R^2 \\ & (R^1)\alpha & \end{array}$$

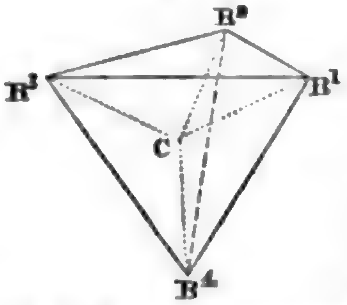
(1920) THE VAN'T HOFF-LE BEL ASYMMETRIC CARBON ATOM HYPOTHESIS.—A system of formulæ based on the arrangement of the symbols in space, instead of in a single plane, to which these objections do not apply, has been proposed by Van't Hoff (*La Chimie dans l'Espace:* P. M. Bazendijk, Rotterdam, 1875; see also Herrmann's adaptation of the same: *Die Lagerung der Atome im Raume*); and similar views have been independently advocated by Le Bel (*Bull. Soc. Chem.*, xxii. 337; comp. *ibid.*, xxiii. 295).

Van't Hoff represents each carbon atom as occupying the centre of a tetrahedron with its four affinities directed towards the four solid angles where the four radicles associated with the carbon atom are situated. Compounds of the forms $C(R)_3R^1$, $C(R)_2(R^1)_2$, and $C(R)_2R^1R^2$ cannot, on this hypothesis, exist in isomeric modifications, as a difference in the relative positions of the various radicles is not conceivable; but if all four radicles are different, two modifications are possible, just as two non-superposable tetrahedra may be formed from the octahedron, the relation of the one to the other being that of an object to its reflected image. The two modifications are represented by Figs. IX. and X.; supposing an observer to be lying along the edge R^1R^3, with his head at R^1, looking towards R^2R^4, he would see R^2 on his right hand in the one case (IX.), and on his left hand in the other (X.)

IX.



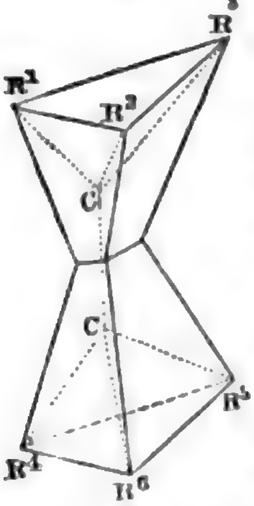
X.



As the tetrahedron representing the combination $CR^1R^2R^3R^4$ has no plane of symmetry, a carbon atom associated with four dissimilar radicles may be termed an *asymmetric* carbon atom. The presence of an asymmetric carbon atom in a formula may be indicated by an italicised *C*.

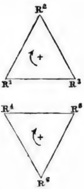
A combination of two carbon atoms associated by a single affinity of each is represented by two tetrahedrons joined together as in Fig. XI.

XI.

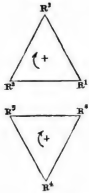


A simpler symbol of such a combination is obtained by supposing the four angles $R^1R^3R^4R^5$ of this Figure to be in the same plane, and folding down the triangles $R^1R^2R^3$ and $R^4R^5R^6$ in this plane, thus producing the Fig. XII. Further, let it be assumed that the system rotates about an axis joining the two carbon atoms. Then it is evident that Figs. XII. and XIII. merely represent the same combination at two phases of rotation; but Figs. XII. and XIV. represent isomerides, since in the one case both groups are rotating in a positive direction, and in the other one in the positive, and the other in the negative direction.

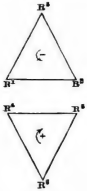
XII.



XIII.



XIV.

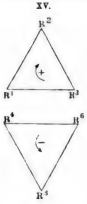


Hence, in the case of a compound containing two singly united asymmetric carbon atoms, four modifications are possible, represented by the Figs. XIII., XIV., XV. and XVI. If the order of rotation $R^1R^2R^3$ be denoted by the symbol + A, and rotation in the opposite direction by the symbol − A, and the rotation of the radicles $R^4R^5R^6$ in like manner by + B and − B, these four modifications are represented by the symbols:

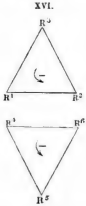
+ A	− A	+ A	− A
+ B	+ B	− B	− B

If, however, only one of the carbon atoms be asymmetric, the number of possible isomerides is reduced to two (Figs. XVII. and XVIII.), since the order of succession of the radicles asssociated with the symmetric carbon atom cannot be varied, and therefore + B = − B.

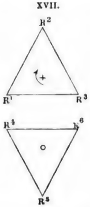
XV.



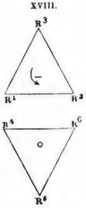
XVI.



XVII.



XVIII.



A compound containing three asymmetric carbon atoms may exist in eight modifications, viz.:

+ A	+ A	+ A	+ A	− A	− A	− A	− A
+ B	− B	+ B	− B	+ B	− B	+ B	− B
+ C	+ C	− C	− C	+ C	+ C	− C	− C

One containing four may exist in sixteen, one containing five in thirty-two modifications: or, generally, a compound of unsymmetrical formula containing *n* asymmetric carbon atoms may exist in $(2)^n$ modifications.

If, however, the compound be represented by a symmetrical formula, the number of possible isomerides is somewhat less. Taking the simplest case of the kind, a body of the formula $C(R^1R^2R^3).C(R^1R^2R^3)$, it is evident that although the radicles associated with each carbon atom are different amongst themselves, the compound nevertheless consists of two similarly constituted halves. This being so, A = B, and it is easy to see that instead of the four isomerides indicated by the symbols

+ A	+ A	− A	− A
+ A	− A	+ A	− A

only three are possible, since

+ A	=	− A
− A	=	+ A

the one being merely the reversal of the other in space.

To take a less simple case such as the following:

$$C(R^1R^2R^3)\ C(R^4R^5)\ C(R^4R^5)\ C(R^1R^2R^3).$$

If the formula were not symmetrical, such a compound should exist in $2^4 = 16$ modifications, viz:

+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−	A
+	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−	B
+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−	C
+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	D
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	

But since A = D and B = C, replacing D by A and C by B, it is evident that the symbols 2, 3, 4, 6, 8, 12, are merely reversals of the symbols 9, 5, 13, 11, 15, 14, so that only the ten following isomeric modifications appear possible:

+	+	−	−	A	+	+	+	+	+	−	A
+	−	+	−	B	+	+	+	−	−	+	B
+	−	+	−	B	+	−	−	+	−	−	B
+	+	−	−	A	−	+	−	−	−	−	A
					−	+	−	−	−	−	A
					+	−	−	+	−	−	B
					+	+	+	−	−	+	B
					+	+	+	+	+	−	A
1	2	3	4		5	6	7	8	9	10	

The number of isomerides possible of a compound represented by a symmetrical formula containing *n* asymmetric carbon atoms is therefore:

$$(2)^{\frac{n}{2}} + \frac{(2)^{n} - (2)^{\frac{n}{2}}}{2}$$

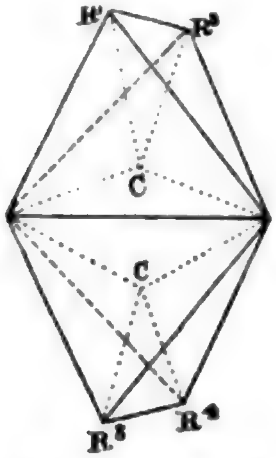
or, since there must always be an even number of asymmetric carbon atoms in a compound of symmetrical formula, we may substitute $2p$ for n; hence

$$(2)^{p} + \frac{(2)^{2p} - (2)^{p}}{2} = (2)^{p-1}(1 + 2^{p})$$

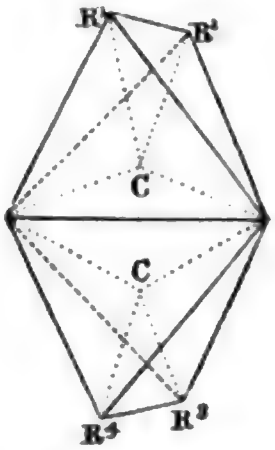
A compound containing two carbon atoms united by two affinities of each is represented by two tetrahedrons joined together by one edge (Fig. XIX.) If the radicles $R^1R^2R^3R^4$ satisfying the remaining four affinities of the carbon atoms are identical, only one such figure can be drawn; but if R^1 be different from R^2, and at the same time R_3 be different from R^4—it being immaterial whether R^1

and R^2 and R^3 and R^4 respectively are different or identical—two such figures can be constructed (XIX. and XX.) in which the radicles R^1R^2 occupy different positions relatively to the radicles R^3R^4.

XIX.



XX.



In other words, a compound of the form $C(R^1R^2){=}C(R^3R^4)$ may exist in two isomeric modifications.

The Van't Hoff hypothesis does not indicate a greater number of isomerides than our present theory in the case of compounds containing carbon atoms united by three affinities of each (acetylene derivatives), or in the case of benzene derivatives.

When the formulæ of the various saturated compounds before mentioned as affording exceptional instances of isomerism are scrutinized, it will be evident that they all contain one or more asymmetric carbon atoms, thus:

Mannitol and dulcitol	$\mathrm{CH_2(OH).(}\mathit{C}\mathrm{H.OH)_4.CH_2(OH)}$
Dextro- and lævo-glucose and galactose	$\mathrm{CH_2(OH).(}\mathit{C}\mathrm{H.OH)_4.COH}$
Saccharic and mucic acid	$\mathrm{COOH\ (}\mathit{C}\mathrm{H.OH)_4.COOH}$
Hydrobenzoin and isohydrobenzoin	$\mathrm{C_6H_5.}\mathit{C}\mathrm{H(OH).}\mathit{C}\mathrm{H(OH).C_6H_5}$
Lactic acid	$\mathrm{CH_3.}\mathit{C}\mathrm{H(OH).COOH}$
Malic acid	$\mathrm{COOH.CH_2.}\mathit{C}\mathrm{H(OH).COOH}$
Tartaric acid	$\mathrm{COOH.}\mathit{C}\mathrm{H(OH).}\mathit{C}\mathrm{H(OH)\ COOH}$

The exceptional instances occurring in the acrylic series and in the $C_nH_{2n-2}(COOH)_2$ series, would also appear to meet with an explanation on Van't Hoff's hypothesis. Whether the isomerism of the terpenes and citrenes, of the camphors, and of a few other compounds, could also be accounted for in a similar way, cannot at present be decided, as we are not yet sufficiently acquainted with their constitution. The sufficiency of the explanation which is apparently afforded by Van't Hoff's hypothesis will be discussed later on.

(1921) CONSTITUTION OF OPTICALLY ACTIVE BODIES.—Since the large majority of crystalline circularly polarizing bodies are destitute of optical activity in the amorphous and liquid states, the property of circular polarization possessed by such bodies must be ascribed to a peculiar arrangement of the molecules, and not to any speciality of constitution of the molecules themselves. The constant correlation of the position of the hemihedral faces on the crystals, and the direction in which the plane of polarization is deflected by a substance, led Pasteur to infer that the molecules are arranged in such crystals in a right- or left-handed spiral; this view has received much support from Sohncke's observation, that by arranging a number of thin plates of optically biaxial mica so that the principal section of each plate is equally inclined (by an angle of 45°, 60°, 90°, or 120°) to that of the previous plate, a combination may be obtained which behaves like an optically active crystal, rotating the plane of polarization either to the right or to the left according to the direction in which the combination is arranged.

Extending this view to the molecules themselves of bodies which are optically active in the amorphous or liquid, but not in the crystalline state, Pasteur inferred that they also were characterized by an absence of symmetry, and that they were similar in constitution to the groups of molecules forming the crystals of bodies active only in the crystalline condition. This, however, is precisely the character of a compound of the form $CR^1R^2R^3R^4$. The four radicles being different will be unequally attracted, and consequently at different distances from the carbon atom, so that the compound will have no plane of symmetry; moreover, the two tetrahedra which represent the two possible modifications of a compound containing a single asymmetric carbon atom, exhibit in relation to an axis drawn parallel to corresponding edges a right-handed screw-like grouping of the radicles in the one case, and a left-handed screw-like grouping in the other. The compound of the one form may therefore be expected to cause the rotation of a plane polarized ray to the right, and the other its rotation to an equal extent in the opposite direction, excepting in the case of the compound being of symmetrical formula, when, if the two equal groups composing it exercise the opposite effect on polarized light, it will be inactive.

Le Bel and Van't Hoff have pointed out as a matter of fact that all optically active bodies of known constitution* contain one or more asymmetric carbon atoms in their formula, as will be evident from the following examples:—

Lactic acid	$CH_3.\mathit{C}H(OH).COOH$
Malic acid	$COOH.CH_2.\mathit{C}H(OH).COOH$
Tartaric acid	$COOH.\mathit{C}H(OH).\mathit{C}H(OH).COOH$
Tartramide	$CONH_2.\mathit{C}H(OH).\mathit{C}H(OH).CONH_2$
Secondary-butylcarbinol (active amylic alcohol)	$CH_3.CH_2.\mathit{C}H(CH_3).CH_2(OH)$
Methethacetic acid	$C_2H_5.\mathit{C}H(CH_3).COOH$
Hydroxyglutaric acid	$COOH.CH_2.CH_2.\mathit{C}H(OH).COOH$
Secondary-butylacetic acid (active valeric acid)	$CH_3.CH_2.\mathit{C}H(CH_3).COOH$
Mannitol	$CH_2(OH).(\mathit{C}H\,OH)_4.CH_2(OH)$
Glucose	$CH_2(OH).(\mathit{C}H.OH)_4.COH$
Saccharic acid	$COOH.(\mathit{C}H.OH)_4.COOH$
Phenylhydroxyacetic (mandelic) acid . . .	$C_6H_5.\mathit{C}H(OH).COOH$

As previously shown, a compound of unsymmetrical formula containing n asymmetric carbon atoms may exist in $(2)^n$ modifications, a compound of the form $C(R^1R^2R^3)$, $C(R^4R^5R^6)$, for example, exhibiting the four modifications

$$1.\ \begin{matrix}+A\\+B\end{matrix}\qquad 2.\ \begin{matrix}+A\\-B\end{matrix}\qquad 3.\ \begin{matrix}-A\\+B\end{matrix}\qquad 4.\ \begin{matrix}-A\\-B\end{matrix}$$

Representing the rotatory power of the group A by the symbol $+A$ or $-A$ and that of the group B by $+B$ or $-B$, the rotatory power of each of these modifications will be as follows:

$$1.\ A+B\qquad 2.—A-B\qquad 3.\ -A+B\qquad 4.\ -A-B$$

Hence 1 and 4 and 2 and 3 will have equal but opposite rotatory powers, and it may be shown that always in the case of compounds of unsymmetrical formula one-half the isomerides are respectively of equal but opposite rotatory power to the other half.

A compound of symmetrical formula, with two asymmetric carbon atoms, may exist in three modifications; the rotatory powers of these will be

$$A+A=2A\qquad A-A=0\qquad -A-A=-2A$$

---

* It is highly probable that this is true of all optically active bodies, since the great majority are compounds of considerable complexity, as for instance the carbohydrates, the glucosides, the alkaloids, the albuminoids, &c.

Two only of the modifications of such a compound, in fact, will manifest optical activity, the two groups of which one is composed compensating each other in their action on polarized light. The three modifications of tartaric acid—dextro-, lævo- and mesotartaric acid—which may be regarded as the three possible modifications of a compound of the formula $\mathrm{COOH}.\mathit{C}\mathrm{H(OH)}.\mathit{C}\mathrm{H(OH)}.\mathrm{COOH}$, illustrate this in a most striking manner.

Whether the mere presence of an asymmetric carbon atom in a compound is sufficient to endue it with optical activity, or whether it is essential that the radicles associated with the carbon atom should be of a particular character and the compound of a particular type, is at present entirely matter for speculation. With reference to this point, however, it is an interesting fact that the simplest known optically active body (lactic acid) contains three carbon atoms.

According to Van't Hoff and Le Bel, if a body which does not contain an asymmetric carbon atom be converted either by substitution or addition into a compound containing one or more asymmetric carbon atoms, it is to be expected that isomerides of equal and opposite rotatory power will be produced in equal quantities, and the product will consequently be inactive. This has been shown actually to be the case, Jungfleisch having found that the tartaric acid prepared artificially from succinic acid is a mixture of racemic and mesotartaric acids, while Le Bel has proved that inactive synthetically prepared methylpropylcarbinol is a mixture of optically active isomerides of opposite rotatory power. Moreover, according to Van't Hoff, there is little hope of obtaining an optically active body from an inactive compound containing asymmetric carbon atoms but of symmetrical formula by destroying its symmetrical character. For example, erythrol (erythrite)

$$\mathrm{CH_2(OH)}.\mathit{C}\mathrm{H(OH)}.\mathit{C}\mathrm{H(OH)}.\mathrm{CH_2(OH)}$$

may be converted by distillation with formic acid into the glycol

$$\mathrm{CH_2(OH)}.\mathit{C}\mathrm{H(OH)}.\mathrm{CH{=}CH_2}$$

and as this is a body of unsymmetrical formula and contains an asymmetric carbon atom, it should by hypothesis be optically active. But it is probable that while the group A of a certain number of erythrol molecules would be attacked, the group $-\mathrm{A}$ of an equal number of other molecules would undergo a like change, so that the product would be an inactive mixture of bodies of equal but opposite rotatory power; thus

$$2\mathrm{CH_2}\underbrace{\mathrm{(OH)}.\mathit{C}\mathrm{H(OH)}}_{\mathrm{A}}.\underbrace{\mathit{C}\mathrm{H(OH)}.\mathrm{CH_2}}_{-\mathrm{A}}\mathrm{(OH)} \qquad \text{would give}$$

$$\mathrm{CH_2}\underbrace{\mathrm{(OH)}.\mathit{C}\mathrm{H(OH)}}_{\mathrm{A}}.\mathrm{CH{=}CH_2} + \mathrm{CH_2{=}CH.CH}\underbrace{\mathrm{(OH)}.\mathrm{CH_2(OH)}}_{-\mathrm{A}}$$

A most important method of discriminating such mixtures of oppositely active bodies has been indicated by Pasteur and Le Bel. Pasteur long ago observed that when a minute organism, the *Penicillium glaucum*, was allowed to vegetate in a dilute solution of racemic acid, it exercised a selective effect, oxidizing the dextro- more readily than the lævotartaric acid, so that the solution, from being inactive, gradually acquired a lævorotatory power. Recently Le Bel has shown (*Compt. Rend.*, lxxxix. 312) that when the inactive amylic alcohol obtained by distilling the ordinary lævorotatory alcohol of fermentation with sodic hydrate is similarly treated, it yields a dextrorotatory amylic alcohol, and that inactive methylpropylcarbinol prepared by the action of nascent hydrogen on methylpropylketone when thus treated yields methylpropylcarbinol of considerable lævorotatory power ($a_{\mathrm{D}} = -12^{\circ}{\cdot}3$ per 220 mm.).

(1922) **PROBABLE INSUFFICIENCY OF THE VAN'T HOFF-LE BEL HYPOTHESIS.**—The differences manifested by the two optically active modifications of tartaric acid would appear to be precisely of the character that might be expected, supposing them to be related in constitution in the manner indicated by the asymmetric carbon atom hypothesis, for in chemical and many of their physical properties they are indistinguishable; they differ only in respect of their crystallographic characters, their pyroelectrical relations, and their behaviour in polarized light, the difference being always of such a character that a particular property is developed to precisely the same extent, but in opposite directions, by the two modifications.

This is very probably true also of the optically active malic acids and of the active camphoric acids, also of the optically active terpenes, citrenes, and camphors; but it is not true with regard to the majority of exceptional instances of isomerism that have been mentioned. The differences noticeable between mannitol and dulcitol, the hydrobenzoins, the glucoses—dextrose, lævulose and galactose—mucic and saccharic acids, certain acids of the acrylic series, malic and fumaric acids, the pyrocitric acids, &c., are so considerable, however, that it does not appear probable that they are related merely in the manner supposed by the Van't Hoff-Le Bel hypothesis.

Again, although the hypothesis appears to afford a very satisfactory explanation of the relationship of the isomeric tartaric acids, there are a number of facts which throw much doubt on its sufficiency as an explanation of the constitution of optically active compounds generally. Thus, malic acid, which manifests a slight lævorotatory power in a pure aqueous solution, acquires an increased lævorotatory power on the addition of boric acid, but is dextrorotatory in presence of nitric acid. It cannot be supposed, in explanation of these phenomena, that the molecule consists of two symmetrical halves + A and − A, and that the rotatory power of the one half alone is influenced by the boric acid and that of the other half by the nitric acid, since malic acid, $COOH.CH_2.\mathit{C}H(OH).COOH$, contains only a single asymmetric carbon atom. Asparagine and aspartic acid and mannitol exhibit a similar behaviour, which is equally difficult to understand. Then the anomalous rotatory dispersive power of aqueous solutions of tartaric acid (Arndtsen, *Ann. Chim. Phys.* 1858, iv. 403) almost necessitates the assumption that the acid forms a compound with water opposite to itself in rotatory power; the formation of a body having a reversed rotatory power as compared with that of the parent substance from a compound like dextrotartaric acid which, according to Van't Hoff's hypothesis, has the constitution 2 A—*i.e.*, is composed of two similar dextrorotatory groups—is, however, not easy to understand. Lastly, whether the inactivity of mannitol—the slight rotatory power which it manifests is probably to be ascribed to the presence of impurity (comp. Müntz and Aubin, *Ann. Chim. Phys.* [5], x. 533)—be regarded as the result of external or internal compensation—*i.e.*, whether it is similar in constitution to racemic or mesotartaric acid—a symmetrical alteration in its composition should not have the effect of converting it into an optically active body, whereas, as a matter of fact, the hexacetate, hexnitrate and hexsulphate prepared from it are powerfully dextrorotatory substances.

The readiness with which many optically active bodies undergo a permanent alteration in rotatory power is also highly remarkable. Thus ordinary tartaric acid may be converted by mere heating into mesotartaric and racemic acid, and in the same way mesotartaric acid may be transformed into racemic acid. Camphoric acid behaves similarly. The hydrogenation of camphor, according to Montgolfier, results in the formation of two distinct camphols, $C_{10}H_{17}.OH$, of equal and opposite rotatory power, both of which, however, give the same dextrocamphor on oxidation.

Probably, however, the most weighty objection that can be raised to the hypothesis is that certainly the majority, if not all, the isomeric compounds which have been mentioned as exceptional instances of isomerism have different energies, as shown by the fact that they differ not only in physical properties, but more particularly in the relative degrees of readiness with which they enter into combination or reaction with other bodies. The mere grouping of the atoms in a positive or negative direction would scarcely result in such a difference.

The question remains whether a slight extension of the hypothesis will not render it capable of including all the phenomena. The kinetic theory of gases seems to be in complete accord with all known facts, and it would appear that we are fully justified in accepting the molecular theory of the constitution of matter (comp. Osborne Reynold, *Trans. Roy. Soc.*, 1879, 727); it is going but a slight step further to suppose that the molecules themselves consist of atoms occupying certain relative mean positions, and that our formulæ are, to a certain extent, correct representations of the relative mean positions of the atoms. Are we not perhaps justified in supposing that there are two classes of isomerides—ordinary isomerides, in which the atoms occupy relatively different positions; and "exceptional" isomerides, in which the atoms occupy relatively similar positions, but in which they are situate at different distances apart?

§ XI. Acids of the Furfuryl Group.

Under this heading a number of acids are conveniently described, which probably are derived from, or more or less closely related to, the compound C_4H_4O, of which furfuraldehyde is a derivative (1662).

(1923) Pyromucic acid: $C_5H_4O_3 = C_4H_3O.COOH$.—This acid is a product of the dry distillation of mucic acid, but it is formed in such small quantity that it cannot well be prepared in this manner; it is also obtained on oxidizing furfuraldehyde either by means of argentic hydrate, or an alcoholic solution of potassic hydrate, the amount obtained by the latter method being equal to one-third the weight of the furfuraldehyde employed (comp. Limpricht, *Ann. Chem. Pharm.*, clxv. 278).

Pyromucic acid crystallizes in colourless plates or needles which melt at 134° (273°·2 F.); it is easily soluble in alcohol and boiling water, but much less soluble in cold water. Ethylic pyromucate, $C_5H_3O_3(C_2H_5)$, crystallizes in plates which melt at 34° (93°·2 F.), and boils at 210° (410° F.).

Pyromucic acid is not acted on by acetic chloride, and when treated with phosphoric pentachloride it yields a chloride which is decomposed by water, and reconverted into pyromucic acid.

On dry distillation of baric pyromucate with soda-lime, a small quantity of a compound of the formula C_4H_4O, termed by Limpricht (*loc. cit.*) *tetraphenol*, is produced; this compound, however, has none of the properties of a phenol: it is a colourless liquid of peculiar odour, boiling at 34° (93°·2 F.), and is not acted on by sodium or by alkalies, but is at once attacked by acids and converted into so-called pyrrol-red.

The behaviour of pyromucic acid on treatment with bromine is of considerable interest. When submitted to the action of dry bromine, it forms a crystalline tetrabromide, $C_5H_4Br_4O_3$, the ethylic salt of which is obtained in a similar manner from ethylic pyromucate; ethylic pyromucate also combines with chlorine, forming a tetrachloride.

Pyromucic acid tetrabromide melts at about 160° (320° F.), but is at the same time decomposed; its ethylic salt melts at 47° (116°·6 F.). Both compounds are very readily reconverted into the parent substances by the action of reducing agents. The former is insoluble in cold water; hot water acts upon it violently, decomposing it with evolution of carbonic anhydride; on oxidation with a dilute solution of chromic acid, it is converted into dibromosuccinic acid. By acting upon pyromucic acid tetrabromide with an alcoholic solution of potassic hydrate, dibromopyromucic acid, $C_5H_2Br_2O_3$, is formed; this acid crystallizes from water in colourless scales, melting at 185° (365° F.); it is a body of considerable stability, resisting the action of a boiling chromic acid solution (Tönnies, *Deut. chem. Ges. Ber.*, xi. 1085).

When bromine is added to an aqueous solution of pyromucic acid, carbonic anhydride is evolved, the colour of the bromine rapidly disappearing until two molecular proportions have been added to a single molecular proportion of the acid; the product, as a rule, is a monobasic acid of the formula $C_4H_4O_3$, which may be extracted by ether, but sometimes a body of the formula $C_4H_3BrO_2$ is obtained instead, the precise conditions under which the one or the other is produced being unknown (Limpricht). The compound $C_4H_4O_3$ crystallizes with difficulty; on adding baric hydrate to its aqueous solution, immediately the latter is neutralized, it becomes yellow, and a yellow precipitate is then thrown down. If the original crude solution of the compound $C_4H_4O_3$ be concentrated on the water-bath, it deposits crystals of fumaric acid; and this acid is also obtained if, after adding bromine, the solution be digested with argentic hydrate: the amount produced is, however, relatively small (comp. Baeyer, *ibid.*, x. 1361). The compound $C_4H_3BrO_2$ crystallizes in white needles, having a camphor-like odour; it melts at 84° (183°·2 F.), and although insoluble in water, readily volatilizes in a current of steam. On reduction, it yields the compound $C_4H_4O_2$, which is a colourless strongly refracting liquid, having a benzene-like odour, insoluble in water; this compound is not altered by concentrated hydrochloric acid or by alkalies, and does not combine with acid sulphites.

When pyromucic acid is submitted to the action of an excess of bromine in presence of water, it is converted into so-called *mucobromic acid* (Schmelz and Beilstein; Limpricht), $C_4H_2Br_2O_3$; this acid is best prepared by adding the bromine as quickly as possible and then boiling the solution for a short time (Jackson and Hill, *ibid.*, xi. 1671). It crystallizes in white glistening plates, melting at 121° (249°·8), easily soluble in alcohol and hot water, but difficultly soluble in cold water. It furnishes a crystalline baric salt of the formula $(C_4HBr_2O_3)_2Ba$, and a corresponding crystalline argentic salt, both of which, however, very readily decompose; ethylic mucobromate crystallizes in rhombic prisms, melting at 51° (123°·8 F.). On warming mucobromic acid with phosphoric pentabromide, a crystalline "acid bromide" of the formula $C_4HBr_3O_2$ is obtained, which melts at 54 (129°·2 F.) This bromide is slowly converted into the acid when boiled with water. A monacetyl derivative, $C_4HBr_2O_3(C_2H_3O)$, is produced on heating the acid with an excess of acetic chloride; it crystallizes in long needles, melting at 54° (129°·2 F.) (Jackson and Hill). Acetic chloride is without action on ethylic mucobromate. The decomposition of mucobromic acid into $\alpha\beta$-dibromacrylic and formic acids by alkalies has already been described (1894). On oxidation with bromine water or nitric acid, mucobromic acid is converted into dibromomaleic acid, $COOH.CBr = CBr.COOH$; this reaction leaves little doubt that it is the aldehyde-acid of the formula $COH.CBr = CBr.COOH$ (Hill, *ibid.*, xiii. 734).

By saturating an aqueous solution of pyromucic acid at 0° (32° F.) with chlorine, then heating it to the boiling-point, again passing chlorine into the cold solution, &c., *mucochloric acid*, $C_4H_2Cl_2O_3$, is obtained, about 40 per cent. of the theoretical amount being formed. This acid crystallizes in rhombic plates, melting at 125° (257° F.); its properties are completely analogous to those of mucobromic acid (Bennett and Hill, *ibid.*, xii. 655).

Mucobromic acid is also formed by the action of bromine on a boiling aqueous solution of dibromopyromucic acid; if, however, a cold solution of the latter be treated with bromine, a compound of the formula $C_4H_2Br_2O_2$ is produced. This body crystallizes from ether in star-like groups of needles, melting at 88° (190°·4 F.); on oxidation with a solution of chromic acid it is converted into mucobromic acid (Tönnies, *ibid.*, xii. 1202).

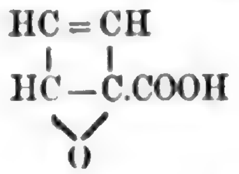
(1924) *Isopyromucic acid:* $C_5H_4O_3$.—This acid is formed together with pyromucic acid on distilling mucic acid. It crystallizes in delicate plates, melting at 82° (179°·6 F.), extremely soluble in water, alcohol, and ether; the aqueous solution is coloured deep green by ferric chloride, whereas a solution of pyromucic acid furnishes a reddish-yellow precipitate with this reagent. It is converted into mucobromic acid by the action of an excess of bromine (Limpricht and Rohde, *Ann. Chem. Pharm.*, clxv. 298).

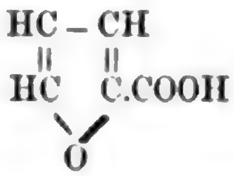
β-Pyromucic acid: $C_5H_4O_3$.—According to Stenhouse (*Proc. Roy. Soc.*, 1871, xx., 81), the acid obtained by oxidation of fucusaldehyde is isomeric with pyromucic acid, as it crystallizes in rhombic plates, melting at 130° (266° F.), instead of in needles; the argentic salt forms long flat needles instead of crystalline scales.

(1925) *Furfuracrylic acid:* $C_7H_6O_3 = C_4H_3O.CH = CH.COOH$.—This acid is obtained by heating furfuraldehyde with acetic anhydride and sodic acetate. It crystallizes from hot water in long thin brittle needles, melting at 135° (275° F.); it has a cinnamon-like odour, and volatilizes in a current of steam; concentrated hydrochloric acid dissolves it, forming a green solution. On treatment of its aqueous solution with sodium amalgam, *furfuropropionic acid*, $C_7H_8O_3$, is produced; this acid melts at 51° (123°·8 F.) (Baeyer, *Deut. chem. Ges. Ber.*, x. 357). On adding a single molecular proportion of bromine to a cold aqueous solution of furfuropropionic acid, and then heating the solution at 65°—70° (149°—158° F.) with the hydrate from six mol. proportions of argentic nitrate, oxidation takes place without the evolution of carbonic anhydride, *furonic acid*, $C_7H_8O_5$, being formed. Furonic acid crystallizes in fine needles, difficultly soluble in cold water, melting at 180° (356° F.). The argentic salt obtained by adding argentic nitrate to a solution of the ammonic salt, has the formula $C_7H_6Ag_2O_5$. By the action of hydriodic acid at 160° (320° F.), furonic acid is converted into hydrofuronic acid, $C_7H_{10}O_5$, which crystallizes in needles melting at 112° (233°·6 F.); but if it be submitted to the action of this acid at about 200° (392° F.), it yields normal pimelic acid (1850), $C_5H_{10}(COOH)_2$ (Baeyer, *ibid.*, x. 695; 1358).

(1926) *Furfurangelic acid:* $C_9H_{10}O_3 = (?)C_4H_3O.CH = CH.C_2H_4.COOH$.—This homologue of furfuracrylic acid is prepared in a similar manner by heating furfuraldehyde with butyric anhydride and sodic butyrate.* It forms colourless, glistening needles, melting at 88° (190°·4 F.); on reduction with sodium amalgam, it yields furfurovaleric acid, $C_9H_{12}O_3$, a colourless oil of unpleasant odour, which may be distilled unchanged. On treatment with bromine and then with argentic hydrate, furfurovaleric acid is converted into butyrofuronic acid, $C_9H_{12}O_5$; this latter acid is readily reduced by nascent hydrogen from sodium amalgam, and when heated with hydriodic acid and red phosphorus at about 200° (392° F.), it is converted into an acid of the formula $C_7H_{14}(COOH)_2$, which is apparently normal azelaic acid (1852) (Baeyer and Tönnies, *ibid.*, x. 1364; Tönnies, *ibid.* xii. 1200).

(1927) CONSTITUTION OF THE FURFURYL COMPOUNDS.—Of the following





two formulæ, which are most in accordance with the general behaviour of pyromucic acid, the first has been put forward by Baeyer as the more probable (*ibid.*, x. 1360). At present there is not sufficient evidence on which to base a final decision, some facts appearing to favour the adoption of the one and some that of the other formula, but on the whole the balance of proof would appear to be in favour of the second. Thus, if the formula of the tetrachloride of ethylic pyromucate be, as Baeyer has suggested, viz.:

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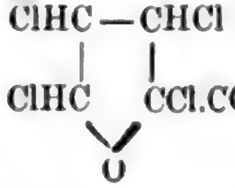
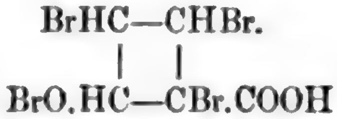
* Isobutyric anhydride does not yield an isomeric acid, but the products of its action on furfuraldehyde in presence of sodic butyrate are carbonic anhydride and furfurobutylene, $C_4H_3O.C_4H_7$.



the second formula would appear to be preferable, as the disruption of carbon atoms united by single affinities by the action of chlorine under conditions such as those which obtain in the formation of this chloride is without precedent. It may, however, be supposed that the formula of the tetrabromide is unsymmetrical, thus:



one-half the bromine entering into combination after the manner that it may be assumed to combine with ethylenic oxide. The fact that furfurin (1662), which probably contains three of the groups C_4H_3O, combines with only six atoms of bromine, tends, to some extent, to support this view. The indifference of pyromucic acid towards acetic chloride and of Limpricht's so-called tetraphenol—which probably is formed from pyromucic acid by the mere displacement of the carboxyl group by hydrogen—towards nascent hydrogen, however, is scarcely in accordance with the assumption that the furfuryl compounds are derivatives of a body of the ethylenic oxide type.

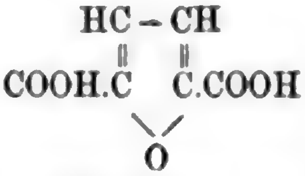
The formation of dibromosuccinic acid on oxidation of pyromucic tetrabromide is explained almost equally well by either formula. This is also true of the production of so-called mucobromic acid by the action of bromine in presence of water on pyromucic acid. Both of these reactions, however, appear rather to favour the adoption of the second of the above formulæ for pyromucic acid. The compound $C_4H_4O_3$, obtained by Limpricht, has been regarded as the half-aldehyde of fumaric acid, $COH.CH{=}CH.COOH$, on account of the formation of this acid on treatment of the crude solution with argentic hydrate, and this view meets with support from the fact that mucobromic acid, which is probably the brominated derivative of the compound $C_4H_4O_3$, has a corresponding formula; but it is not impossible that fumaric acid and the compound $C_4H_4O_3$ are products of distinct reactions, and that the latter is derived from previously formed dibromosuccinic acid.

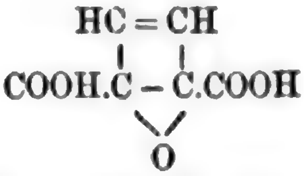
Apart from the question of the constitution of the $C_4H_4O_3$ (furfuryl) group, there can be no doubt that in furfuracrylic acid the group $C_2H_2.COOH$ occupies the position of the COOH group in pyromucic acid; no other formula would account for its conversion into normal pimelic acid.

The formula of furfurangelic acid is not so well established; if the azelaic acid formed by its reduction be the normal acid, it undoubtedly has the formula $C_4H_3O.CH{=}CH_2.CH_2.COOH$; but it is possible that it has the formula $CH_3.CH_2.C(C_4H_3O).COOH$. The high melting-point of the azelaic acid produced favours the former assumption.

(1928) *Dehydromucic acid:* $C_6H_4O_5 = C_4H_2O(COOH)_2$.—To prepare this acid mucic acid is heated with a solution of hydrobromic acid saturated at 0° (32° F.) for eight hours at 130°—140° (266°—284° F.): the amount produced is equal to about 30 per cent. of the mucic acid employed. It crystallizes in long glistening needles, difficultly soluble in cold, more easily soluble in hot water. Baric dehydromucate, $C_6H_2O_5Ba$, the most characteristic salt of the acid, crystallizes with either 3 or 6 molecules of water. Ethylic dehydromucate crystallizes from alcohol in colourless prisms, melting at 47° (116°·6 F.); it is not acted on by acetic anhydride. Dehydromucic acid, if carefully heated, sublimes unchanged without melting, but if submitted to dry distillation it is entirely resolved into carbonic anhydride and pyromucic acid. On treatment with nascent hydrogen, it yields two isomeric acids of the formula $C_6H_6O_5$ (Heinzelmann, *Ann. Chem. Pharm.* cxciii. 184; Seelig, *Deut. chem. Ges. Ber.*, xii. 1081).

There can be little doubt that dehydromucic acid is closely related in constitution to pyromucic acid; the following formulæ may be suggested as the most probable:





(1929) *Meconic acid:* $C_7H_4O_7$.—Meconic acid occurs in opium chiefly in combination with the alkaloids, and may be precipitated as baric or calcic salt from the aqueous extract by the addition of baric or calcic chloride. To prepare the acid, crude calcic meconate is gradually added to a mixture of 6 pts. ordinary hydrochloric acid and 20 pts. boiling water, the mixture being frequently shaken, and kept at a temperature somewhat below 100° (212° F.) until the whole is dissolved; if necessary, the liquid is then rapidly filtered through a linen bag; on cooling, the acid is deposited, but in more or less coloured crystals: it may be partially purified by dissolving these in as little hot water as possible and then adding hydrochloric acid, being much less soluble in dilute hydrochloric acid than in water, and finally is rendered colourless by recrystallization from boiling water.

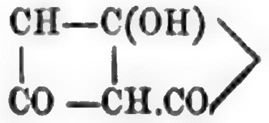
Meconic acid crystallizes in micaceous scales of the formula $C_7H_4O_7 + 3OH_2$, readily soluble in water and alcohol; the crystals are rendered anhydrous by heating at 100° (212° F.).

The general behaviour of meconic acid is that of a dibasic acid, but it also yields trimetallic derivatives, a tri-argentic derivative, $C_7HAg_3O_7$, for example, being thrown down as a yellow precipitate on the addition of argentic nitrate to a solution of the acid neutralized with ammonia. A solution of meconic acid or of a meconate is coloured blood-red by ferric chloride; the colour is not discharged on boiling, or on the addition of dilute hydrochloric acid, or of a dilute solution of mercuric chloride (distinction from acetates and thiocyanates). If an alcoholic solution of the acid be saturated with hydrochloric acid, a monethylic and diethylic salt, both of which are crystalline, are produced; a triethylic salt cannot be obtained, however. By acting on a solution of meconic acid with sodium amalgam until a portion of the neutralized liquid is not coloured by ferric chloride, hydromeconic acid is formed; this acid, according to Korff (*Ann. Chem. Pharm.*, cxxxviii. 191), probably has the formula $C_7H_{10}O_7$, but it does not crystallize, neither does it furnish crystalline salts; this acid is not acted on either by bromine or by nitric acid, but on distillation decomposes entirely (comp. Ihlée, *ibid.* clxxxviii. 41).

(1930) *Comenic acid*, $C_6H_4O_5$, is produced on heating meconic acid at about 120° (248° F.) and by prolonged boiling of an aqueous or hydrochloric acid solution of this acid. It crystallizes in anhydrous prisms or laminæ, requiring more than 16 times their weight of boiling water to dissolve them. It yields both mono- and dimetallic salts, but is apparently a monobasic acid, forming only a monethylic salt; like that of meconic acid, its solution is coloured red by ferric salts. When submitted in aqueous solution to the action of bromine or chlorine, it yields bromo- and chlorocomenic acids, $C_6H_3BrO_5$ and $C_6H_3ClO_5$, but at the same time a considerable proportion undergoes oxidation to oxalic acid, &c. It combines with nascent hydrogen (Korff).

(1931) *Pyromeconic* (?) *acid:* $C_5H_4O_3$.—This isomeride of pyromucic acid is formed on submitting either meconic or comenic acid to dry distillation. It crystallizes from water in large colourless prisms, melting at 117° (242°·6 F.), easily soluble in cold water and alcohol; it boils at 225° (437° F.) almost without decomposition (Ost, *Jour. pr. Chem.* [2], xix. 177). It affords a blood-red coloration with ferric salts. Although its solution exhibits only a faint acid reaction, pyromeconic acid forms well-characterized metallic derivatives of the formula $C_5H_3O_3M'$, and also a peculiar class of derivatives of the formula $C_5H_3O_3M' + C_5H_4O_3$. Thus, if an excess of an alcoholic solution of potassic hydrate be added to a hot saturated alcoholic solution of the acid and the liquid allowed to cool, a crystalline mass of the potassic derivative $C_5H_3O_3K$ is obtained. On digesting a warm solution of the acid with baric carbonate, carbonic anhydride is evolved, and as the solution cools the compound $(C_5H_3O_3)_2Ba + 2C_5H_4O_3$ crystallizes out in glistening needles (Ihlée, *Ann. Chem. Pharm.*, clxxxviii. 31); the normal barium derivative, $(C_5H_3O_3)_2Ba + 3OH_2$, is formed on adding baric chloride to a solution of the acid in a large excess of ammonia (Ost). These derivatives are all exceedingly unstable, and decompose on boiling their solutions; if the acid is heated with an excess of baric hydrate solution, it rapidly decomposes, formic acid being the chief product. It does not furnish an ethylic salt; but on digestion with acetic chloride, it is converted into the monacetyl derivative $C_5H_3O_3(C_2H_3O)$. On passing hydrochloric acid gas into a solution of pyromeconic acid in pure ether, white crystals of a compound of the formula $C_5H_4O_3HCl$ are produced; a similar compound with sulphuric acid may be obtained by adding sulphuric acid; these bodies are at once resolved into their generators by water (Ost). Pyromeconic acid does not combine with bromine, but if left in contact with it is gradually converted into bromopyromeconic acid, $C_5H_3BrO_3$. Nitropyromeconic acid, $C_5H_3(NO_2)O_3$, may be obtained by acting on an acetic acid solution of the acid with nitric acid; it crystallizes in yellow prisms; on reduction it is converted into amidopyromeconic acid, $C_5H_3(NH_2)O_3$. Nitropyromeconic acid yields a number of characteristic metallic derivatives of the formula $C_5H_2(NO_2)O_3M'$, but does not appear capable of forming derivatives corresponding to the "acid" pyromeconates: these compounds are all highly unstable. Pyromeconic acid is readily acted on by nitrous acid, and apparently is converted into a highly unstable nitroso-derivative of the formula $C_5H_3(NO)O_3 + C_5H_4O_3$; on treatment with sulphurous acid this compound takes up two atoms of hydrogen, and on extracting the product with hot chloroform, decomposition takes place, pyromeconic acid going into solution, oxypyromecazonic acid, $C_5H_5NO_4$, being left. This last mentioned body crystallizes from water in white needles; in general behaviour it closely resembles pyromeconic acid, forming two series of metallic derivatives, and being very readily decomposed by alkalies; submitted to the prolonged action of tin and hydrochloric acid, it loses an atom of oxygen, being converted into pyromecazonic acid, $C_5H_5NO_3$, which closely resembles the parent compound in its properties, and differs greatly from the isomeric amidopyromeconic acid, although, like the latter, it yields an intense indigo-blue colour with ferric chloride. The metallic derivatives of oxy- and of pyromecazonic acids very readily oxidize on exposure to air, forming blue and violet compounds (Ost).

It will be evident that the so-called pyromeconic acid differs totally from pyromucic acid in its general behaviour; the following formula would appear to some extent to express its reactions:



ADDITIONS, CORRECTIONS AND CROSS REFERENCES.

(1031) *Fractional Distillation.*—An improved apparatus for: Le Bel and Henninger, *Ber.** **7**, 1084. Observations on: F. D. Brown, *J. C. S. Trans.* 1879, 547; 1880, 49; Thorpe, *ibid.* 1879, 544.

(1032) *Ultimate Analysis of Carbon Compounds.*—On the occlusion of hydrogen by copper: Johnson, *Journ. C. S.* **29**, 178; *Trans.* 1879, 232; Lietzenmayer, *Ber.* **11**, 306. Potassium chromate as a substitute for copper: Perkin, *C. S. Trans.* 1880, 121. Platinum as a substitute for cupric oxide: Kopfer, *Ber.* **9**, 1377. The simultaneous determination of carbon, hydrogen, and nitrogen: Hempel, *Zeits. Anal. Chem.* 1878, 409.

(1041) *Determination of the Halogens in Carbon Compounds.*—Volhard: *Ann.* **190**, 40; Schiff, *ibid.* **195**, 293.

(1051) *Determination of Vapour Density.*—Improvements in Hofmann's method: *Ber.* **9**, 1304; Thorpe, *C. S. Trans.* 1880, 146. According to Brühl (*Ber.* **12**, 197), Hofmann's method is not available at temperatures above 220°. A new simple method of determining vapour density: V. and C. Meyer, *Ber.* **11**, 2253.

(1100) *Hydrocyanic Acid.*—Ammonic formate, according to Andreasch (*Ber.* **12**, 973), yields only water and formamide, $HCO.NH_2$, on distillation (comp. p. 92). On the polymerisation of hydrocyanic acid, see *C.R.* **89**, 310.

(1121) *Diferrous Dipotassic Ferricyanide.*—According to Skraup (*Ann.* **186**, 371), this substance may be formed either by precipitating potassium ferrocyanide with a ferric salt or potassium ferricyanide with a ferrous salt. On treatment with a ferrous salt, it is converted into triferrous ferricyanide or Turnbull's blue, Fe_5Cy_{12}, a ferric salt converting it into the compound $Fe_7\ Cy_{18}$.

(1162) *Normal Heptane.*—The exudation from *Pinus sabiniana* has been shown by Thorpe to consist almost entirely of pure normal heptane (*C. S. Trans.* 1869, 296).

(1166) *Perchlorination and Perbromination of Paraffins.*—Comp. ft. note, p. 392, and Krafft and Merz, *Ber.* **8**, 1045, 1296; Krafft, *Ber.* **9**, 1085; **10**, 801; Merz, *Ber.* **9**, 1049, 1506; **11**, 2244.

(1171) *Trichloromethane.*—The formation of this compound on distillation of wood spirit with bleaching powder is apparently to be ascribed to the presence of acetone in the former. The production from alcohol probably involves the prior formation of trichloracetic acid (comp. Schmitt and Goldberg (*Jour. pr. Chem.* [2] **19**, 393.)

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* *Ber.* Berichte der deutschen chemischen Gesellschaft zu Berlin.
C. S. Trans. Journal of the Chemical Society. Transactions.
C. S. Journ. Journal of the Chemical Society.
C. R. Comptes rendus de l'Academie des Sciences, Paris.
Ann. Liebig's Annalen der Chemie und Pharmacie.

(1175) *Haloid Derivatives of Ethane.*—Comp Staedel and Denzel, *Ann.* **195**, 180.

(1188) *Dibromopropanes.*—On the most favourable conditions for the conversion of allylic bromide into α-dibromopropane, see Erlenmeyer, *Ann.* **197**, 169.

(1202) *Nitroparaffins.*—For additional information on these compounds, see *Ann.* **180**, 111; **181**, 1; *Ber.* **9**, 384—396, 701; **10**, 2083; **12**, 622, 1883.

(1207) *Dinitropropane.*—γ-Dinitropropane, $CH_3.CH_2.CH(NO_2)_2$, isomeric with the δ-dinitropropane, $CH_3.C(NO_2)_2.CH_3$, described in this paragraph, is obtained as potassium derivative by the action of potassic nitrite on potassium bromonitropropane, $CH_3.CH_2.CKBr(NO_2)$. It is sharply distinguished from the isomeride by the power which it has of exchanging an atom of hydrogen for metals (ter Meer, *Ann.* **181**, 19).

(1220) *Cyanoform.*—Pfankuch's statements with regard to this compound appear to have been untrue (comp. Kolbe, *Jour. pr. Chem.* [21] **17**, 287.)

(1226) *Properties of Olefines.*—On the action of water on olefines, see Butlerow, *Ann.* **180**, 245; comp. ft. note, p. 414. The somewhat contradictory and irregular results of different observers who have studied their behaviour on oxidation appear to have been in a great measure due to the employment of impure materials, or to the occurrence of secondary changes. Recent observations indicate that in the main the action probably consists in the conversion of the olefine in the first place into the corresponding dihydric alcohol, which then undergoes oxidation in the usual manner (comp. Butlerow, *Ann.* **173**, 375; **189**, 70; Jawein, **195**, 256; Pawlow, *Ann.* **196**, 125; Zeidler, *Ann.* **197**, 243; Hecht, *Ber.* **11**, 1152).

(1227) *Isomeric and Homologous Olefines.*—The olefines noticed in the following paragraphs which are not included in the table on pp. 184—185 have to be inserted.

(1231) *Isobutylene.*—On the action of nitric acid on, see Hartinger, *Ann.* **193**, 366.

(1232) *Amylene.*—It appears now to be placed beyond doubt that the crude amylene from ordinary fermentation amylic alcohol is a mixture of no less than four isomeric olefines, viz., $C_3H_7{}^{\beta}.CH:CH_2$, $C_2H_5.C(CH_3):CH_2$, $CH(CH_3):C(CH_3)_2$ and $C_3H_7.{}^{\delta}CH:CH_2$ or $C_2H_5.CH:CH.CH_3$ (comp. pp. 448, 450, 517, 835, and *Ann.* **197**, 253; *Ber.* **10**, 1905, 2058). The first and second of these are primary derivatives of the two alcohols which are the well recognized constituents of ordinary amylic alcohol; the third is formed from the first and second by isomeric change. The origin of the fourth is at present obscure; it has been suggested, however, that fusel oil contains normal primary amylic alcohol.

The iodide formed by combining α-methylethylethylene from diethylcarbinol (p. 195) with hydriodic acid has the formula $CH_3.CHI.C_3H_7{}^{\alpha}$ (*Ann.* **179**, 313).

(1233) *Hexylene.*—Hexylene from secondary hexylic iodide from mannite has the formula $C_3H_7.{}_{\alpha}CH:CH.CH_3$ (Hecht, *Ber.* **11**, 1152). On tetramethylethylene, $C(CH_3)_2:C(CH_3)_2$, ethyl-α-dimethylethylene, $C_2H_5.C(CH_3):CH(CH_3)$, and ethyl-β-dimethylethylene, $C_2H_5.CH:C(CH_3)_2$ see Pawlow, *Ann.* **196**, 122; and Jawein, *Ann.* **195**, 253. These olefines boil respectively at 73°, 71°, and 66°.

(1234) *Heptylene.*—The following additional heptylenes have been described: methyl-α-diethylethylene, $CH_3.C(C_2H_5):CH.C_2H_5$ (b. p. 90°—95°) and trimethylethylethylene, $(CH_3)_2C:C(CH_3)(C_2H_5)$ (b. p. 75°—80°) (Pawlow, *Ann.*

188, 124) methylisobutylethylene, $CH_3.CH{:}CH.C_4H_9{}^{\beta}$ (Rohn, *Ann.* **190**, 314); methyl-δ-butylethylene, $CH_2{:}C(CH_3)(C_4H_9)^{\delta}$ (Butlerow, *Ann.* **177**, 185.)

(1235) *Octylene.*—Normal octylene or α-hexylethylene, $CH_2{:}CH.C_6H_{13}\alpha$, from normal octylic iodide, is said to boil at 122°—123° (Mösslinger, *Ann.* **185**, 53. The octylene from methylhexylcarbinol doubtless has the formula $CH_3.CH{:}CH.C_5H_{11}\alpha$ (comp. 399). Diisobutylene (comp. p. 835).

(1240) *Haloid Derivatives of Ethylene.*—Comp. Denzel, *Ann.* **195**, 205. A number of chloro- and bromo- derivatives of ethylene and other olefines combine directly with oxygen, forming chlorides or bromides of haloid derivatives of acids of the acetic series; thus dibromethylene, $CH_2{:}CBr_2$, yields monobromacetic bromide, $CH_2Br.COBr$ (Demole, *Ber.* **11**, 315, 1302; **12**, 2245; comp. Henry, *Ber.* **12**, 1838).

(1244) *Chlorobromopropylenes.*—The supposed propylene derivatives prepared from so-called croton-chloral (p. 206) are doubtless propane derivatives (comp. p. 397).

(1248) *Acetylene.*—According to Lagermark and Eltekoff (*Ber.* **12**, 6031), Berthelot's supposed vinylic alcohol is really crotonic aldehyde (comp. Zeisel, *Ann.* **191**, 366), as suggested at p. 213.

(1249) *Cuprous Acetylide.*—Blochmann states (*Ann.* **173**, 176) that after drying over calcic chloride this compound corresponds in composition to the formula $C_2H_2Cu_2O$ (? $HC{:}C.Cu.Cu.OH$) and the analogous silver derivative to the formula $C_2H_2Ag_2O$.

(1254) *Valerylenes.*—Isopropacetylene boils at 28°—30°, and on oxidation yields isobutyric and acetic acids and acetone (*Ber.* **10**, 1102, 2249; **11**, 1939). Methylethylacetylene, $CH_3.C{:}C.C_2H_5$, boils at 51°—52°, and yields acetic and propionic acids on oxidation (*Ber.* **10**, 1904, 2057). On the action of the haloid acids on isoprene, see Bouchardat, *C.R.* **89**, 1117.

(1255) *Hexoylene.*—The bromide of the hexoylene from secondary hexylic iodide from mannite is convertible into a methylpropylacetylene $CH_3.C{:}C.C_3H_7$, which boils at 80°—83°, and on oxidation yields acetic and butyric acids (Hecht, *Ber.* **11**, 1050).

Diallyl.—This hydrocarbon yields chiefly succinic acid on oxidation with potassic permanganate (Sorokin, *Ber.* **12**, 2374).

(1262) *Hydrocarbons of the* C_nH_{2n-4} *series.*—Two additional hydrocarbons of this series have been described, vinylallylethylene $C_2H_3.CH{:}CH.C_3H_5$ (*Ann.* **185**, 144) and cantharene, C_8H_{12} (*Ber.* **12**, 577). The latter is obtained from cantharidin; it boils at 134°, and absorbs oxygen with great avidity; on oxidation it is converted into orthotoluic acid.

(1265) *Artificial Terpenes.*—The hydrocarbon obtained by Bauer and Verson yields neither cymene nor terephthalic acid (Tgolessoff, *Ber.* **12**, 14869), and therefore differs totally from the terpenes. According to Bouchardat (*C.R.* **86**, 654), not only isoprene but also (crude) valerylene from (crude) amylene is partially converted into a hydrocarbon of the formula $C_{10}H_{16}$ when heated in sealed tubes at about 250°. The product has all the properties of terpilene, the hydrocarbon obtained by splitting off the elements of two mols. hydrochloric acid from the terpene dihydrochlorides (comp. p. 234).

(1268) *Terpene Hydrochlorides.*—Probably a liquid monohydrochloride does not exist, the supposed liquid isomeride of the solid hydrochloride being apparently a mixture of the solid mono- and dihydrochlorides and cymene (comp. Atterberg, *Ber.* **10**, 1202; Tilden, *Ber.* **12**, 1131). On the action of sodium on the terpene hydrochlorides, see Montgolfier, *Ann. Chim. Phys.* [5] **19**, 145.

(1271) *Terebene.*—The supposed terebene of Deville and Riban is impure inactive camphene (Armstrong and Tilden, *C. S. Trans.* 1879, 733).

(1275) *Nitrosoterpenes.*—See Tilden and Shenstone, *C. S. Journ.* **31**, 554.

(1276) *Terpene monohydrates.*—See Flavitzsky, *Ber.* **12**, 2354.

(1284) *Compounds present in Coal Tar.*—The existence of the following compounds, besides those mentioned on p. 251, has been established. Acetonitrile, $CH_3.CN$, ethylic alcohol (*Ber.* **10**, 2227), orthoxylene (*Ber.* **10**, 1010), fluoranthene, $C_{15}H_{10}$ (*Ann.* **193**, 142; **200**, 1), carbazol, $C_{12}H_9N$ (*Ann.* **163**, 256; **167**, 125), and phenylnaphthylcarbazol, $C_{16}H_{11}N$ (*Ber.* **12**, 341, 2242).

(1291) *Dippel's oil.*—On the constituents of this oil: see Weidel (*Ber.* **12**, 1989; Weidel and Ciamician, *Ber.* **13**, 65).

(1292) *Benzene.*—On the action of hydriodic acid on benzene and its homologues, see Wreden *Ann.* **187**, 153; Berthelot, *Ann. Chem. Phys.* [5] **15**, 150; comp. (1296). On the action of chlorous acid on benzene, comp. ft. note, p. 795.

From "but inasmuch," line 7, to "Benzene," line 16, and the included fig. on p. 263, should be cancelled, and the words "whereas only three are known" should be inserted after "exist" on line 7. The alternative symbol there given is that proposed by Körner (*C. S. Journ.* 1876, **29**, 240), who appears entirely to have overlooked the fact that this symbol involves the existence of only two isomeric di-derivatives of benzene. That this is the case will readily be seen on constructing Körner's symbol with the aid of three knitting-needles or pieces of wire, a cork, and string: each of the carbon atoms to which the hydrogen atoms 2, 4 and 6, are respectively attached, it will be evident, is similarly situated relatively to the carbon atom 1, and to the carbon atoms 3 and 5. Comp. p. 389; also Japp, *C. S. Trans.* 1880, 89.

(1294) *Homologues of Benzene.*—The following have to be added to the list on p. 278:—1:3-methylethylbenzene, $CH_3.C_6H_4.C_2H_5$ (b. p. 158°—159°), *Ann.* **192**, 198; 1:4-methylisopropylbenzene, $CH_3.C_6H_4.C_3H_7{}^{\beta}$ (b. p. 171°·5), *Ber.* **12**, 429; γ-butylbenzene, $C_6H_5.CH(CH_3)(C_2H_5)$ (b. p. 171°), comp. ft. note, p. 342; pentamethylbenzene, $C_6H(CH_3)_5$, *Ber.* **12**, 329; hexmethylbenzene, $C_6(CH_3)_6$, *Ber.* **12**, 329, *C.R.* **87**, 260; 1:4 propylisopropylbenzene, $C_3H_7{}^{a}.C_6H_4.C_3H_7{}^{\beta}$ (b. p. 212°).

(1300) *Xylene.*—On the separation of the three isomeric xylenes, see Jacobsen, *Ber.* **10**, 1009.

(1301) *Isopropylbenzene.*—Comp. Liebmann, *Ber.* **13**, 45.

(1302) *Cymene.*—The synthesis of this hydrocarbon from normal propylic bromide and parabromotoluene has been verified by Jacobsen (*Ber.* **11**, 2049). Jacobsen has also confirmed Kraut's remarkable observation that cymene is formed on boiling cuminylic alcohol (1481)—an isopropylic compound—with zinc dust; as well as Nencki and Ziegler's statement (p. 280) that cymene is converted into cuminic acid on oxidation in the body (*Ber.* **12**, 1512). According to Etard (*C.R.* **90**, 534), cuminic aldehyde is obtained on treatment of the product of the action of chromic chloride, CrO_2Cl_2, on cymene with water. No explanation of these remarkable instances of isomeric change has as yet been given.

(1302) *Durene.*—Reuter has shown (*Ber.* **11**, 31) that this hydrocarbon has the constitution expressed by fig. II., p. 295.

(1304) *Propylisopropylbenzene.*—This hydrocarbon, obtained by the action of zincic ethide on the chloride $C_3H_7.C_6H_4.CH_2Cl$ from cuminylic alcohol, yields propylbenzoic acid, isomeric with cuminic acid, and homoterephthalic acid $COOH.C_6H_4.CH_2.COOH$ on oxidation (Paterno and Spica, *C. S. Journ.* **34**, 138).

(1306) *Hydrocarbons* $C_{15}H_{24}$.—The suggestion that these hydrocarbons are tripropyl-derivatives of benzene is doubtless incorrect; probably, like the terpenes, they are of peculiar constitution.

(1313) *Hexabromobenzene.*—Comp. Gessner, *Ber.* **9**, 1506.

(1317) *Chlorobenzenes.*—On the isomeric tri- and tetrachlorobenzenes, all the possible modifications of which are now known, see Beilstein and Kurbatow, *Ann.* **192**, 228.

(1322) *Iodobenzene.*—This may be prepared by adding iodine chloride to benzene containing a small quantity of aluminic chloride (Greene, *C.R.* **90**, 40).

(1344) *Trinitrobenzene.*—Comp. Hepp. *Ber.* **9**, 402.

(1346) *Nitrotoluene.*—Crude nitrotoluene is a mixture of the para-, ortho-, and meta- compound (*Ber.* **12**, 343).

(1353) *Nitro-haloid Derivatives of Toluene.*—On the action of chlorine and bromine on the heated mononitrotoluenes, see Wachendorff, *Ann.* **185**, 259; Greiff, *Ber.* **13**, 288.

(1356) *Action of Reagents on Benzene, &c.*—The meta- as well as the para- and ortho- derivative is formed by the action of nitric and of sulphuric acid on toluene (Claesson and Wallin, *Ber.* **12**, 1848), and also on treating aniline sulphate dissolved in an excess of sulphuric acid with nitric acid (Huebner, *Ber.* **10**, 1716). This should be noted in the table on p. 337.

(1357) *Cinnamene.*—On homologues of this hydrocarbon, see Perkin, *C. S. Journ.* **32**, 660.

(1367) *Chloronaphthalenes.*—Comp. p. 498. Much attention has recently been paid to the investigation of the naphthalene derivatives, and no less than eight isomeric dichloronaphthalenes are now known. They will be found fully described in the art. "Naphthalene," in Watts' *Dictionary*, vol. viii., pt. 2.

(1376) *Homologues of Diphenyl.*—On the formation of these by Zincke's method, comp. sec. 5, p. 772.

(1389) *Constitution of Anthracene.*—For a proof that in both C_6- groups of anthracene two atoms of hydrogen in the ortho-position are displaced, see v. Pechmann, *Ber.* **12**, 2125. It is probable that the conversion of dibromanthraquinone into alizarin does not merely involve the displacement of the bromine atoms by two hydroxyl groups, and therefore this reaction does not afford a reliable determination of the constitution of dibromanthraquinone (comp. Perkin, *Chem. News*, **41**, 45).

(1392) *Constitution of Phenanthrene.*—Comp. Japp, *C. S. Trans.*, 1880, 86.

(1402) *Triphenylmethane.*—This hydrocarbon is a product of the conjoint action of aluminic chloride and trichloromethane on benzene (Friedel and Crafts, *C. R.* **84**, 1450.)

(1407) *Dinaphthyls.*—Three isomeric dinaphthyls are now known (Watson Smith, *C. S. Journ.* 32, 559; *Trans.* 1879, 224).

(1410) *Dinaphthylethylene.*—Comp. Grabowski, *Ber.* **11**, 298.

(1413) *Tetraphenylmethane.*—Comp. sec. 5, p. 772.

(1416) *Review of the Hydrocarbons.*—With reference to the action of hypochlorous acid on propylene, and of sulphuric acid on amylene, discussed on p. 401, comp. pp. 451, 462, 835. Ossipoff's conclusions appear to have been based upon an insufficient examination of the products (comp. Wischnegradsky, *Ber.* **10**, 404).

(1419) *Tertiary Carbinols.*—Comp. p. 562.

(1421) *Formation of Tertiary Carbinols.*—Comp. p. 771. By action of water on mono-haloid derivatives of paraffins, see Niederist, *Ann.* **186**, 388; **196**, 349.

(1422) *Diagnosis of Carbinols.*—Meyer's method appears only to be available for the lower terms of the series. It answers with normal primary octylic alcohol, but fails with secondary hexylic iodide (Gutknecht, *Ber.* **12**, 622).

(1426) *Methylic Alcohol.*—Thorpe gives 65°·2 as the boiling point of this alcohol (*C. S. Trans.* 1879, 544) .On the action of chlorine on methylic alcohol, comp. p. 461.

(1427) *Ethylic Alcohol.*—On the synthesis of this alcohol from ethylene, comp. p. 188.

(1430) *Isomeric change in the Propyl Series.*—On the action of water on propylenic bromide, &c. (ft. note, p. 437), comp. Eltekoff *Ber.* **11**, 989; Flavitzky, *Ber.* **11**, 1940.

(1435) *Isomeric change in Butyl Series.*—According to Meyer, Barbieri and Foster (*Ber.* **10**, 130), Linnemann's statement that normal butylamine nitrite yields isoprimary butylic alcohol is incorrect; the products are normal buylene, normal primary butylic alcohol and secondary butylic alcohol. Comp. Brauner, *Ber.* **12**, 1877. For "secondary," line 15 from bottom p. 442, read "isoprimary."

(1438) *Amylic Alcohols.*—On optically active and inactive amylic alcohols, see Le Bel, *Bull. Soc. Chim.* **31**, 104.

(1439) *Propylmethyl Carbinol.*—Comp. p. 991.

(1444) *Dimethylisopropyl Carbinol.*—This alcohol boils at 117°, Pawlow, *Ann.* **196**, 123.

(1448) *Tertiary Heptylic Alcohols.*—Comp. p. 562.

(1454) *Table of Carbinols of Ethylic Series*, pp. 458, 459, 460.—Alter b. p. of methylic alcohol to 65°·2, and diff. of b. p. between methylic and ethylic alcohols to 13°·2. Also b. p. of dimethylisopropylcarbinol to 117°, and diff. between it and dimethyl-β-butycarbinol to 13°. Insert tertiary alcohols described on p. 562.

(1457) *Allyldimethyl Carbinol.*—Comp. *Ann.* **185**, 151. Three homologues of this alcohol are now known:—allyldiethylcarbinol (b. p. 155°—156°); allyldipropylcarbinol (b. p. 192°—193°); and methylbutallylcarbinol, $CH_3.CH(OH).CH_2.C_3H_5$ (b. p. 138°—139°) (*Ann.* **196**, 109, 113; *C. S. Trans.* 1878, 53).

(1461) ***Methyldiallyl Carbinol.***—Three homologues of this alcohol also have been prepared:—diallylcarbinol (b. p. 151°); diallylpropylcarbinol (b. p. 195°); and diallylisopropylcarbinol (b. p. 182°—185°) (*Ann.* **185**, 129, 169; **193**, 362; *Ber.* **12**, 689, 2374).

(1462) *Homologues of Phenol.*—Several of the phenols noticed in the following paragraphs have to be added to the list on p. 469.

(1463) *Preparation of Phenols.*—Comp. Degener, *Jour. pr. chem.* [2] **17**, 394; **20**, 300; Meyer, *Ber.* **8**, 1074.

(1466) *Phenoquinone.*—Comp. note to 1690.

(1471) *Bromophenols.*—Tribromophenol is converted into the compound $C_6H_2Br_3.OBr$ by the action of bromine water; on warming with concentrated sulphuric acid until it melts, this body forms tetrabromophenol $C_6HBr_4.OH$ (Benedikt, *Ann.* **199**, 127).

(1479) *Xylenols or Xenols.*—Jacobsen has shown (*Ber.* 11, 17) that the crystalline xenol described on p. 492 is derived from paraxylene; it therefore has the constitution [$OH : CH_3 : CH_3 = 1:2:5$]. Paraxenol melts at 74°·5, and boils at 211°·5. The supposed xenol from mesitylenesulphonic acid is mesitol (1480). Metaxylene yields two isomeric sulphonic acids, which are converted into corresponding metaxenols by fusion with potassic hydrate; that from the sulpho-acid, which is the chief product, has the constitution, [$OH:CH_3:CH_3 = 1:2:4$] and is liquid; the isomeride, [$OH:CH_3:CH_3 = 1:2:6$,] is crystalline and has the same melting and boiling point as paraxenol. Orthoxenol, [$OH:CH_3:CH_3 = 1:3:4$.] melts at 61° and boils at 225°.

(1480) *Propylphenols. Pseudocumenol.*—Both propyl- and isopropylbenzene yield isomeric sulphonic acids, which are converted into corresponding phenols by fusion with potassic hydrate. The propylphenols are both liquid; the para-compound boils at 232°, the ortho- at 226°. The isopropylphenol which is the chief product melts at 61° and boils at 229°; the isomeric ortho-compound is liquid, and boils at 227° (Paterno and Spica, *Gazz. Chim.* **6**, 535; **7**, 216).

Pseudocumenol, $C_6H_2(CH_3)_3.OH$, from pseudocumenesulphonic acid, melts at 69° and boils at 240° (Reuter, *Ber.* **11**, 29). Mesitol boils at 220°.

(1483) *Cholesterin.*—Cholesterin is converted into a dinitro-derivative by the action of concentrated nitric acid (*Ber.* **12**, 224). On the behaviour of cholesterin on oxidation, see *Ber.* **10**, 82, 232; **11**, 1941.

(1489) *Anthrols.*—By reducing anthraquinonemonosulphonic acid with hydriodic acid, and fusing the resulting anthracenesulphonic acid with potassic hydrate, an anthrol $C_6H_4{:}C_2H_2{:}C_6H_3(OH)$ is produced different from either of those described by Linke, whose observations Liebermann has been unable to verify (*Ber.* **12**, 592). By heating anthraquinone with hydriodic acid and phosphorus, an isomeric phenol, $C_6H_4{:}C_2H(OH){:}C_6H_4$, so-called anthranol, is obtained (Liebermann and Topf, **9**, 1201). Chrysazin (1705), when treated in like manner, yields a dihydric alcohol of the formula $C_6H_4{:}C_2H(OH){:}C_6H_3(OH)$ (*Ber.* **10**, 606; **11**, 1610). Two isomerides of the latter, of the formula $C_6H_3(OH){:}C_2H_2{:}C_6H_3(OH)$, have been obtained from the isomeric disulphonic acids prepared from anthracene (*Ber.* **11**, 1615; **12**, 185).

(1496) *Glycol.*—On the preparation of glycol, see Niederist, *Ann.* **196**, 354. Comp. Eltekoff, *Ber.* **11**, 989; Flavitzky, *Ber.* **11**, 1256, 1940.

(1499) *Methyl Glycol.*—Comp. note to 1530.

(1502) *Propylmethyl Glycol.*—This glycol yields acetic and normal butyric acid on oxidation as required by the formula $C_3H_7.CH(OH).CH(OH).CH_3$ (Hecht, *Ber.* **11**, 1154).

(1505) *Orcinols.*—It would probably be better to term the 1:3 dihydric phenols *orcinols* rather than resorcinols as suggested in the ft. note, p. 519.

(1508) *Pentabromoresorcinol.*—This body doubtless has the formula $C_6HBr_3(OBr)_2$ and the corresponding chlorine derivative and the homologous compounds from orcinol are similarly constituted (comp. Benedikt, *Ann.* **196**, 127).

(1517) *Constitution of Orcinol.*—Supposing orcinol to be a resorcinol derivative, the relative position of the methyl and hydroxyl groups may be [$OH{:}OH{:}CH_3 = 1{:}3{:}5$ or $1{:}3{:}4$] or [$OH{:}CH_3{:}OH = 1{:}2{:}3$]. The tendency which it exhibits to form tri-derivatives; its conversion into a dinitroso-derivative (Stenhouse and Groves, *C. S. Journ.* **31**, 544); and the formation from it of two dialdehydes favour the assumption that it has the constitution [$OH{:}OH{:}CH_3 = 1{:}3{:}5$].

(1525) *Hydrobenzoin.*—The conclusion that hydro- and isohydro-benzoin must both be represented by the formula $C_6H_5.CH(OH).CH(OH).C_6H_5$ has been entirely confirmed by further investigation (Zincke and Breuer, *Ann.* **198**, 115, 141; comp. 1665, 1680, 1919 and *Ber.* **11**, 65, 1396; **13**, 641). Both furnish benzil, $C_6H_5.CO.CO.C_6H_5$, on oxidation with nitric acid. When submitted to the action of PCl_5, hydrobenzoin yields two chlorides of the formula $C_{14}H_{12}Cl_2$, one of which melts at 192°, the other at 94°; and the former of these chlorides only is obtained from isohydrobenzoin. When submitted to the action of twenty per cent. sulphuric acid, they each furnish diphenethaldehyde, $(C_6H_5)_2CH.COH$, together with a crystalline substance of the empirical formula $C_{14}H_{12}O$; the products of this formula from the two alcohols are isomeric, however, but apparently the isomerism is similar in character to that which obtains between the parent alcohols.

At line 15 from bottom, p. 536, insert the word "much" before "lower," and at line 13 insert the words "melts at only a 14° higher" temperature, instead of at a higher temperature.

(1527) *Anthraquinol.*—Comp. note to 1489.

(1530) *Glycerol.*—Sodium glycerol (p. 539) yields methylglycol, among other products, on dry distillation; it suffices to distil a mixture of equal molecular proportions of glycerol and sodium hydrate (*Ber.* **12**, 1872).

According to Fitz (*Ber.* **11**, 42, 1892), *Bacillus subtilis* ferments glycerol with formation of ethylic alcohol, 100 grammes of glycerol yielding from 25–30 grammes of alcohol; an allied *Bacillus*, somewhat larger in size, however, produces normal butylic alcohol (p. 546). It may also be fermented to normal propylic alcohol (*Ber.* **13**, 36).

(1534) *Pyrogallol.*—The formation of anthragallol (1706, p. 807) with the aid of pyrogallol would appear to indicate that in this latter the three OH groups are relatively in the positions 1 : 2 : 3 (comp. p. 810), but the occurrence of isomeric change in such a reaction is by no means improbable.

(1535) *Phloroglucol.*—This alcohol is formed on fusing phenol or resorcinol with sodic hydrate, the latter yielding nearly 70 per cent. of its weight; the former only about 20 per cent. (Barth and Schreder, *Ber.* **12**, 417. 503).

(1544) *Isodulcitol.*—Comp. Behrend, *Ber.* **11**, 1353.

(1554) *Cupric reducing power of Carbohydrates.*—Soxhlet, in a recent paper (*Jour. pr. Chem.* [2] **21**, 227–289), entirely condemns the gravimetric process for the estimation of dextrose. He finds that the amount of cupric salt reduced by this and most other carbohydrates is largely influenced by the concentration of the solution and by the presence of an excess of the cupric salt. Thus, ·5 grm. dextrose in a 1 per cent. solution reduces 105·2 cc. of Fehling's solution of ordinary strength, but only 101·1 cc. of the same solution diluted with 4 vols. of water; its reducing power is greater in presence of an excess of the oxidizing agent. The same is true of invert sugar and lactose; the reducing power of milk sugar is not altered by this amount of dilution, and is less affected by an excess of cupric salt; the reducing power of amylon, on the other hand, is not affected by the employment of an excess of Fehling's solution of ordinary strength, but diluting the solution has the effect of increasing it. From these results Soxhlet argues that it is not legitimate to suppose that the carbohydrates are capable of reducing cupric salts in a definite molecular ratio (comp. p. 581). The facts he adduces, however, scarcely warrant so sweeping a conclusion; the products of oxidation, whatever their nature, may be expected under all circumstances to exert a certain amount of action on the cupric salt, and it does not appear probable that, if it were not the case, the approach to a definite molecular proportion would be so constant, or so near, as it actually is. The reducing power of dextrose being taken as 100, that of the other carbohydrates in 1 per cent solutions for Fehling's (f), Knapp's (k), and Sachsse's (s) solutions (comp. pp. 582, 607) is given in the first three columns of the following table, the number of cc. of Knapp's (K) and Sachsse's (S) solutions which are reduced by 1 gram of each in a 1 per cent. solution being shown in columns 4 and 5:

	f.	k.	s.	K.	S.
Cane sugar	100·0	100·0	100·0	—	—
Invert sugar	96·2	99·0	124·5	502·5	376·0
Lævulose	92·4	102·2	148·6	508·5	449·5
Milk sugar	70·3	64·9	70·9	322·5	214·5
Inverted do.	96·2	90·0	85·5	448·8	258·0
Lactose	93·2	83·0	74·8	413·0	226·0
Amylon	61·0	63·8	65·0	317·5	197·6

1 gram of dextrose reduces 497·5 cc. of Knapp's and 302·5 cc. of Sachsse's solu-

tion. These solutions contain almost the same amounts of mercury, but very different amounts of alkali.

(1559) *Lactose.*—According to Soxhlet, the app. sp. rot. power in a 10 per cent. solution of α-lactose is $[\alpha]_D = 81^\circ{\cdot}5$, which is a considerably lower value than that given by Fudakowski. Soxhlet's observations lend support to the conclusion that ordinary dextrose is one of the products of the hydrolysis of milk sugar.

(1564) *Cane Sugar.*—On the app. sp. rot. power of cane sugar in aqueous solutions, see Tollens and Schmitz, *Ber.* **10**, 1403, 1414. On the sp. gr. of cane sugar and maltose in solution, see Brown and Heron, *C. S. Trans.* 1879, 602, 618. Cane sugar is slowly inverted by digestion with malt extract (Brown and Heron, op. cit. p. 609).

(1565) *Milk Sugar.*—Omit the fig. 2 before $C_{12}H_{22}O_{11}$, line 8 from bottom, p. 611. On some properties of milk sugar, see Mills and Hogarth, *R. Soc. Proc.* **28**, 273. On its cupric reducing power comp, *Ber.* **11**, 2076.

(1566) *Amylon or Maltose.*—On the cupric reducing power and app. sp. rot. power of this carbohydrate, comp. Soxhlet, Brown and Heron, and O'Sullivan, *C. S. Trans.* 1879, 770. Omit the fig. 2 before $C_{12}H_{22}O_{11}$, line 8 from top, p. 613. Diastase solution is without action on amylon (Brown and Heron).

(1570) *Synthesis of Carbohydrates.*—According to Demole (*Ber.* **12**, 1935), the octacetate obtained by the action of acetic anhydride on dextrose (comp. p. 580) yields on treatment with alkali a carbohydrate of the formula $C_{12}H_{22}O_{11}$, having all the properties of that prepared by Gautier from dextrose. By acting on the mixture of glucoses from milk sugar with acetic anhydride, an octacetate of the formula $C_{12}H_{14}O_3(C_2H_3O_2)_8$ is produced, which has all the properties of that prepared directly from milk sugar (Demole). On the acetates prepared from various carbohydrates, see Franchimont, *Ber.* **12**, 1938; Herzfeld, *Ber.* **13**, 265. Peligot states (*C.R.* **89**, 918) that among the products of the action of calcic hydrate on dextrose is a crystalline body of the formula $C_{12}H_{22}O_{11}$, which is destitute of cupric reducing power, unfermentable, unaltered by cold concentrated sulphuric acid, and but little attacked by nitric acid; in crystalline form and many of its properties, this body closely resembles mycon (1568; comp. Berthelot, *C.R.* **89**, 965).

(1571) *Starch.*—On the solubility of starch in water and on the properties of starch paste, see Brown and Heron, *C. S. Trans.* 1879, 596. The experiments of O'Sullivan on the action of malt extract on starch have been extended by Brown and Heron, who have arrived at somewhat different conclusions. Assigning the app. sp. rot. power $[\alpha]_j = 150^\circ$ to amylon (maltose) and $[\alpha]_j = 216$ to amylin (dextrin), and a cupric reducing power of 61 to amylon—values calculated on the assumption that the solid matter in solution has the sp. gr. ·0386—they also conclude that the results obtained are compatible with the hypothesis that amylon and amylin alone are produced. They find, however, that even cold malt extract acts rapidly on cold starch paste, the relative amounts of amylon and amylin (deduced from the observation of the cupric reducing power and app. sp. rot. power) produced under these circumstances, or at temperatures not above 60°, being in accordance with the equation $(C_6H_{10}O_5)_{20} + 8OH_2 = 8C_{12}H_{22}O_{11} + (C_6H_{10}O_5)_4$. If the malt extract be heated to 66°, a smaller proportion of amylon is produced—viz., $3C_{12}H_{22}O_{11}:(C_6H_{10}O_5)_{14}$; if the extract be heated to 75°, or if malt extract heated to 66° and rendered alkaline with sodic carbonate, be employed, the proportions are $2C_{12}H_{22}O_{11} : (C_6H_{10}O_5)_{16}$. And if malt extract heated to 66°, and made very slightly alkaline with sodic hydrate, be used, the proportions are $C_{12}H_{22}O_{11} : (C_6H_{10}O_5)_{18}$. Malt extract has no action on amylon, but on digestion with dilute sulphuric acid this carbohydrate is entirely converted into *ordinary* dextrose. These results may be explained on the assumption that, as pointed out on p. 656, starch has a very high molecular weight—viz., $C_{120}H_{200}O_{100} = (C_6H_{10}O_5)_{20}$, and that under the influence of the malt extract it undergoes gradual simplification, C_{12}–groups being split off and forming amylon, the residue in each case constituting an "amylin." On this hypothesis the "amylins" formed at different stages differ in molecular weight; the difference in their behaviour with iodine lends some support to this view, but on the other hand they all appear to have the same sp. rot. power, and to be otherwise identical. O'Sullivan, in a recent paper (*C. S. Trans.* 1879, 770), in which he upholds and extends his former observations, adduces additional facts in opposition to this view that the different "amylins" are different terms in a series of polymerides. It is highly probable that amylon and "amylin" are not the only products of the action of malt extract on starch, but that bodies intermediate in character are also formed (comp. Herzfeld, *Ber.* **12**, 2120; Soxhlet, *Jour. pr. Chem.* [2] **21**, 2707); their production is readily accounted for on the above hypothesis if it be supposed that the elements of water are added on to the starch molecule, and that a change takes place somewhat similar to that involved in the conversion of ethylenic oxide into glycol. The whole question of the constitution of starch and its transformations is, however, one of extreme difficulty, and one which no doubt will not be set at rest without much further experimental investigation.

According to Musculus and Mering (*Bull. Soc. Chem.*, **31**, 105), saliva and pancreatic fluid also convert starch into amylin and amylon, and also gradually transform the latter into dextrose. Brown and Heron (*private communication*) have verified these observations for pancreatic juice, which they find is capable of slowly converting amylon into dextrose, although it is unable to induce the inversion of cane sugar. The small intestine, especially that portion where the so-called Peyer's glands are situate, furnishes a secretion which, although very slow in its action on starch, very rapidly converts amylon into dextrose, and also inverts cane sugar.

Synanthrose.—Dieck and Tollens (*Ann.* **198**, 228) have shown that the so-called synanthrose of Popp, or, as they term it, lævulin, has the empirical composition $C_6H_{10}O_5$ (comp. p. 641).

(1575) *Glycogen.*—According to Musculus and Mering (*loc. cit.*), glycogen resembles starch in yielding dextrin and amylon on treatment with saliva or malt extract. Bernard's conclusions with regard to the amount of "glucose" in blood (p. 644) from various parts of the body are disputed by Pavy (*R. Soc. Proc.* **26**, 314, 346).

(1589) *Ethers of the $C_nH_{2n+1}.O.C_nH_{2n-1}$ series.*—On the action of sulphuric acid on, see Eltekoff, *Ber.* **10**, 1902. *Vinylethylether*, $C_2H_5.O.C_2H_3$, see Wislicenus, *Ann.* **192**, 106. This ether boils at 35°·5; on decomposition with dilute sulphuric acid, it yields ethaldehyde and ethylic alcohol.

(1594) *Anethol.*—On the synthesis of this compound and of isomeric and homologous ethers, see Perkin, *C. S. J.* **32**, 668; *C. S. Trans.*, 1878, 211.

(1596) *Propylenic Oxide.*—The oxide obtained from the chlorhydrin $CH_2Cl.CH_2.CH_2(OH)$ boils at 50° (Reboul, *Ann. Chem. Phys.* [5] **14**, 453).

(1605) *Pyrogallol ether-alcohols*—Comp. note to 1699.

(1606) *Glucosides.*—*Glycyrrhizin*, according to Habermann (*Ann.* **197**, 105), is the acid ammonic salt of a nitrogenous acid, *glycyrrhizic acid*, and has the formula $C_{44}H_{62}NO_{18}(NH_4)$.

Helicin.—This glucoside may be prepared by the action of so-called acetochlorhydrose (p. 580) on the potassium derivative of salicylic aldehyde, $C_6H_4(OK).COH$, Michael, *C.R.* **89**, 355.

Sinalbin, acording to Will and Laubenheimer (*Ann.* **199**, 150), analogous in constitution to potassic myronate (p. 697), being resolved by the action of myosin into sinalbin thiocyanate $C_7H_7O.NCS$, glucose and sinapine sulphate, $C_{16}H_{23}NO_5.H_2SO_4$.

(1634) *Amidoethylic Acohol.*—On the various products of the action of hydrocyanic acid on this compound, see Erlenmeyer, *Ann.* **200**, 120; comp. 1775, 1780.

(1647) *Heptaldehyde.*—On the preparation of from castor oil, see Krafft, *Ber.* **10**, 2034.

(1658) *Protocatechnic Aldehyde.*—An isomeric aldehyde is obtained by the combined action of chloroform and alkali on resorcinol, and a homologue from orcinol (*Ber.* **10**, 2210; **12**, 9991).

(1661) *Homologues of Benzaldehyde.*—On the formation of cumic aldehyde from cymene, see note to 1302. The production of an acid of much higher melting point than cumic acid by oxidation of propylisopropylbenzene appears to afford confirmation of the conclusion that cumic aldehyde is an isopropyl derivative. Phenethaldehyde, $C_6H_5.CH_2.COH$, is produced, together with a compound of the empirical formula C_8H_8O, on heating phenylglycol, $C_6H_5.CH(OH).CH_2(OH)$, with 20 per cent. sulphuric acid. This glycol is prepared from the corresponding bromide from cinnamene; on oxidation, it yields mandelic acid and small quantities of benzoylcarbinol, $C_6H_5.CO.CH_2(OH)$, and benzoylformic acid, $C_6H_5.CO.COOH$, (*Ber.* **10**, 1004, 1486; **11**, 1399; **13**, 635).

(1662) *Furfuraldehyde.*—On the constitution of, see 1927.

(1669) *Phthaldehyde.*—The supposed aldehyde from phthalic chloride appears from recent researches of Heppert to have the formula $C_6H_4\left\{\begin{matrix}CH_2\\CO\end{matrix}\right\}O$; the acid formed from it by the action of alkalis has the corresponding formula $C_6H_4(CH_2.OH).COOH$. Phthalid, as this substance is more appropriately termed, does not combine with acid sulphites. Phthalic chloride probably corresponds in constitution to phthalid (*Ber.* **11**, 237).

(1671) *Formation of Ketones.*—According to Gustavson (*Ber.* **11**, 2151), aluminic chloride unites with benzene, toluene, &c., forming compounds such as $6C_6H_6{:}Al_2Cl_6$, and these apparently play an important part in the reactions realized by Friedel and Crafts (p. 772).

(1672) *Action of Nitric Acid on Ketones.*—The supposed nitro-derivatives of acids of the acetic series formed on treatment of ketones of the $CO(C_nH_{2n+1})_2$ series with nitric acid are apparently "dinitro-paraffins." Thus the supposed nitropropionic acid from dipropylketone (p. 776) is probably identical with the "dinitropropane" of ter Meer (Chancel, *C.R.* **86**, 1405). On nitroso-derivative of ketones, see p. 915.

(1678) *Ketones of the* $(C_nH_{2n+1})_2CO$ *series.*—On the ketones of the form $CH_3.CO.C_nH_{2n+1}$ containing 13, 15, 17 and 19 carbon atoms, see Krafft, *Ber.* **12**, 1664.

(1687) *Camphor.*—Comp. pp. 976, 979.

(1689) *Quinhydrone.*—The formula $C_{12}H_{10}O_4$ for this substance has been confirmed by Nietzki, *Ber.* **12**, 1779. Resorcinol also combines with quinone, forming an isomeride of quinhydrone.

(1690) *Phenoquinone.*—The formula of this compound, according to Nietzki, is $C_{18}H_{16}O_4$ and not $C_{18}H_{14}O_4$; *i.e.*, it contains the elements of 1 mol. of quinone and 2 mols. of phenol.

(1699) *Cedriret.*—The substance in beech-tar from which cedriret is derived, according to Hofmann, has the formula $C_8H_{10}O_3 = C_6H_3(OCH_3)_2\,OH$. Beech tar also contains a methylpyrogalloldimethylin and the compound $C_{11}H_{16}O_3$ referred to on p. 800 is apparently a propylpyrogalloldimethylin, $C_3H_7.C_6H_2(OCH_3)_2.OH$. The diethylin $C_6H_3(OC_2H_5)_2.OH$ yields an ethylcedriret on oxidation (*Ber.* **11**, 329, 798, 1455; **12**, 1371, 2216).

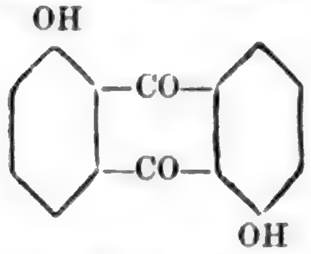
(1705) *Isomerides of Alizarin.*—Line 17 from bottom p. 804, substitute $2-3'$ for (?) $2'-3$ or $2'-2$.

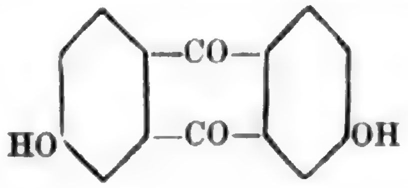
Chrysazin may readily be prepared from anthracene-*a*-disulphonic acid, either by converting this into the corresponding dihydroxyanthracene which is then oxidized, or by oxidizing the sulpho-acid and then fusing the resulting anthraquinonedisulphonic acid with potassic hydrate (Liebermann and Boeck, *Ber.* **11**, 1613; **12**, 182, 1287).

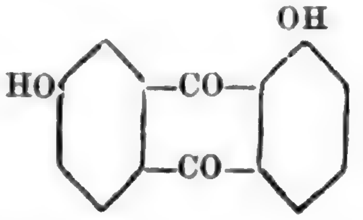
Anthraflavone, according to the later researches of Schunck and Roemer (*Ber.* **11**, 969), is a mixture of three isomerides, the product from 100 pts. metahydroxybenzoic acid consisting of 30 pts. anthraflavic acid, 4 – 5 pts. metabenzbioxyanthraquinone and 2 pts. anthrarufin. The second of these, already partially described, does not yield colours with mordants; on fusion with potassic hydrate it yields isopurpurin, being much more readily acted upon than anthra- or iso-anthraflavic acid. The acetyl derivative melts at 199°. Anthrarufin may be much more readily obtained from anthracene-*β*-disulphonic acid in the same way that chrysazin is formed from the *a*-acid (*Ber.* **11**, 1176, 1613; **12**, 182, 1287). It crystallizes in yellow prisms, melting at 280°; it does not yield colours with mordants; on treatment with nitric acid it forms a tetra-nitro-derivative; its acetyl derivative melts at 245°. It is converted into the same trihydroxyanthraquinone as chrysazin when fused with potassic hydrate; and like chrysazin, if heated with potassic hydrate at a temperature somewhat below that at which the trihydroxy-compound is formed, it furnishes a mixture of salicylic and methydroxybenzoic acid.

Line 16 from top, p. 809, the reference should be, Seuberlich. *Ber.* **10**, 38.

(1710) *Constitution of Anthraquinone Derivatives.*—Three dihydroxyanthraquinones may theoretically be derived from metahydroxybenzoic acid, and not two as stated on p. 810, where one of the figures (the first) is incorrectly printed, they are represented by the following symbols:—







The formation of salicylic and metahydroxybenzoic acid on fusing anthrarufin with potassic hydrate can only be explained on the assumption that anthrarufin is represented by the first of these figs. (Liebermann and Dehnst, *Ber.* **12**, 1293). From the fact that anthraflavic acid is the chief product, and on account of its formation from anthraquinone, it can hardly be doubted that its constitution is represented by the second fig., and the third therefore must be regarded as representative of metabenzbioxyanthraquinone. Isoanthraflavic acid not improbably has the constitution indicated by fig. 1, p. 810; and chrysazin either corresponds to fig. 3, p. 810, or contains the hydroxyl groups in the positions $3'$—1, since it yields the same acids as anthrarufin on fusion with potassic hydrate.

(1711) *Phenanthraquinone.*—See Japp, *Chem. News*, **41**, 170.

(1715) *Constitution of Quinones.*—Comp. Japp, *C. S. Trans.* 1880, 86.

(1723) *Formic Acid.*—Soda-lime rapidly absorbs carbonic oxide at a temperature of 200°—220°, forming sodic formate (Merz a. Tibiriça, *Ber.* **13**, 23; Geuther, *Ber.* **13**, 3237.

(1729) *Diamylene.*—Comp. ft. note with note to 1232.

(1732) *Higher Homologues of Acetic Acid.*—It has long been remarkable that scarcely any of the higher terms containing an uneven number of carbon atoms were known; the blank has recently been filled up by the preparation of the acids containing 11, 13, and 15 carbon atoms by oxidation of the ketones referred to in the note to 1678 (Krafft, *Ber.* **12**, 1664). These acids melt respectively at 28°·5, 40°·5 and 51°; and boil under a pressure of about 100 mm. at 212°·5, 236° and 257°. Margaric acid boils under this pressure at 277°.

(1744) *Ethereal Salts.*—The phenomena attending the formation of ethereal salts have been further studied by Menschutkin, who has extended his observations to many other alcohols and acids besides those mentioned in this section (comp. *Ann.* **195**, 334; **197**, 193; *Ber.* **12**; 665, 2168; **13**, 162).

(1840) *Malonic acid.*—The ethylic salt of this acid, like ethylic acetoacetate, readily exchanges one of its atoms of hydrogen for sodium when submitted to the action either of sodium or of sodic ethylate. The resulting monosodium derivative is acted upon by haloid compounds, such as the moniodoparaffins, furnishing derivatives of the form $CHX(COOC_2H_5)_2$, which also are capable of exchanging an atom of hydrogen for sodium; and the sodium derivative thus produced may then be converted into compounds of the form $CXY(COOC_2H_5)_2$ by treatment with haloid compounds. The ethereal salts formed in this manner mostly yield corresponding acids on saponification; these acids decompose when heated, evolving carbonic anhydride, derivatives of acetic acid of the forms $CH_2X.COOH$ and $CHXY.COOH$ being produced.

Ethylic malonate is readily acted upon by chlorine, and converted into the chlorinated derivative $CHCl(COOC_2H_5)_2$; this is converted into potassic tartronate, $CH(OH)(COOK)_2$, on treatment with potassic hydrate. The derivatives of ethylic malonate of the form $CHX(COOC_2H_5)_2$ behave similarly. Ethylic chloromalonate and ethylic sodiummalonate react to form the compound $(COOC_2H_5)_2CH.CH(COOC_2H_5)_2$. Lastly, ethylic sodiummalonate and the sodium derivatives of the malonates of the form $CHX(COOC_2H_5)_2$ are converted by nitrous acid into corresponding nitroso-compounds, so that the analogy between ethylic malonate and acetoacetate is complete (Conrad; Conrad and Bischoff, *Ber.* **12**, 249, 1236; **13**, 595).

(1864) *Malic acid.*—Although a weak solution of ordinary malic acid is lævorotatory, a concentrated solution is dextrorotatory, the variation in rotatory power being expressed by the equation:

$$[\alpha]_D = 5{\cdot}891 - {\cdot}08959q,$$

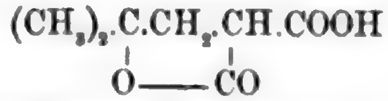
where q is the weight of water in 100 parts of solution, 5·891 being the specific rot. power of the anhydrous acid. Sodium malate exhibits a similar behaviour, its rotatory power being expressed by the equation

$$[\alpha]_D = 15{\cdot}202 - {\cdot}3322 + {\cdot}0008184q^2$$ (Schneider, *Ber.* **13**, 620).

In this respect, malic acid manifests considerable analogy with dextrotartaric acid, very concentrated alcoholic solutions of which, according to Arndtsen, are lævorotatory. These facts meet with an explanation on the assumption that the acid forms a compound with the solvent, and that the acid and its compound with the solvent are bodies of opposite rotatory power.

(1876) *Diaterebic acid.*—This acid and terebic acid would appear to have the following formulæ (Bredt. *Ber.* **13**, 748).

$(CH_3)_2C(OH).CH_2.CH(COOH)_2$



$$(CH_3)_2.\underset{\displaystyle O}{C}.CH_2.\underset{\displaystyle CO}{CH}.COOH$$

(1883) *Desoxalic acid.*—The formula of this acid as printed is incorrect; it should be $C_5H_6O_8$.

INDEX.

Absinthol, 467
Absolute alcohol, 426
Acenaphthene, 357
,, brom-, 358
,, hexabromide, 358
Acenaphthalene, 365
Acetal, 680
,, dichlor-, 681
,, monobrom-, 681
,, monochlor-, 681
,, trichlor-, 681
Acetenylbenzene, 343
Acetates, 826
Acetic bromide, 852
,, chloride (acetylic chloride), 852
,, ,, action of, 86
,, cyanide, 853
,, disulphide, 856
,, iodide, 852
,, peroxide, 856
Acetone, 778
,, action of hydrocyanic acid on, 779
,, chlorobromo-, 782
,, dichlor-, 781
,, ,, chloride, 159
,, diiodo-, 783
,, hexabrom-, 783
,, hexachlor-, 782
,, homologues of, 783
,, monochlor-, 205, 781
,, nitroso-, 915
,, pentabrom-, 782
,, pentachlor-, 782
,, tetrachlor-, 782
Acetonitrile, dibromonitro-, 177
,, diiodonitro-, 177
,, dinitro-, 177
,, trinitro-, 177
Acetonylurea, 780
Acetophenone, 785
Acetyl, bromide, 852
,, chloride, 852
,, cyanide, 853
,, iodide, 852
Acetylene, 209, 1002,
,, chlor-, 965
,, dibromide, 213
,, dichloride, 212
,, diphenyl- (tolane), 381
,, dipotassium-, 214
,, disodium-, 214
,, ditolyl-, 382
,, ethylphenyl-, 369.
Acetylene, homologues of, 215
,, ,, constitution of, 216
,, metallic derivatives of, 214, 1002
,, phenyl-, 343
,, series, table of hydrocarbons of, 208
,, sodium-, 214
,, tetrabromide, 212
Acetylenenaphthalene, 365
Acid, abietic, 239
,, aceconitic, 980
,, acetic, 824
,, ,, higher homologues of, 836, 1012
,, acetoacetic, 906
,, acetoformic or pyruvic, 904
,, acetonic, 895
,, β-acetopropionic (lævulinic), 917
,, acetorthocoumaric, 762
,, acetylene-dicarboxylic, 983
,, aconic, 973
,, aconitic, 979
,, acrylic, 955
,, ,, brom-, 965
,, ,, chlor-, 965
,, adipic, 932, 977 *note*
,, ,, dibrom-, 935
,, ,, monobrom-, 935
,, æscinic, 688
,, æsculic, 701
,, allylacetic, 961
,, amides, 59
,, amidoacetic (glycocine), 866
,, ,, camphoric, 977
,, ,, formic, or carbamic, 979
,, ,, hydroxyacetic, 901
,, ,, malonic, 935
,, ,, propionic (alanine) 738
,, ,, pyromeconic, 999
,, amygdalic, 688
,, anchoic (lepargylic), 933
,, angelic, 959
,, anhydrides, 60
,, ,, of the acetic series, 853
,, anthraflavic, 804
,, ,, diacetyl-, 804
,, ,, tetrabromo-, 804
,, anthraquinone-carboxylic, 382
,, aposorbic, 949
,, arachidic, 839
,, aspartic, or asparaginic, 936
,, azelaic, or anchoic, 933

Acid, behenic, 839
,, behenolic, 982
,, benzamidacetic, or hippuric, 867
,, benzilic, or diphenylglycolic, 787
,, benzoleic, or hydrobenzoic, 982
,, benzylselenious, 714
,, brassic, 964
,, brassylic, 934
,, bromacrylic, 965
,, bromanilic, 797
,, bromides, 59
,, bromitaconic, 972
,, bromocitraconic, 972
,, bromocrotonic, 967
,, bromofumaric, 971
,, bromomaleic, 971
,, bromomethracrylic, 966
,, bromonaphthalic, 358
,, bromopyromeconic, 999
,, butylolactic, 895
,, butyric, normal, 829
,, ,, secondary, 830
,, caïncic, 690
,, camphic, 977
,, campholic, 977
,, camphoric, 974
,, ,, constitution of, 979
,, camphoronic, 977
,, capric, 837
,, caproic, or hexylic isoprimary, 834
,, ,, ,, normal, 834
,, ,, ,, secondary, 834
,, ,, ,, tertiary, 834
,, ,, ,, from pyroterebic acid, 293
,, caprylic, or octylic, iso-secondary, 835
,, ,, ,, normal, 835
,, carbacetoxylic, 906
,, carbamic, 879
,, carbonic, 876
,, carbolic (phenol), 475
,, carbuvic, 928
,, carminic, 690
,, cerotic, 144, 839
,, chloracrylic, 965
,, chloranilic, 796
,, chlorides, 59
,, ,, action of, 86
,, chloritaconic, 972
,, chloritamalic, 970
,, chlorocitraconic, 972
,, chlorocitramalic, 970
,, chlorocrotonic, 966
,, chloromethacrylic, 966
,, chloromuconic, 951
,, chlorotoluic, 319
,, chrysophanic, 808
,, cimicic, 962
,, cinnamenylacrylic, 768
,, citraconic, 969
,, ,, bromo-, 972
,, ,, chloro-, 972
,, citramalic, 949
,, citratartaric, 949
,, citric, 952

Acid, comenic, 998
,, convolvulic, 692
,, crotaconic, 971
,, crotonic or β-methacrylic, 957
,, ,, bromo-, 977
,, ,, chloro-, 966
,, cuproycanic, 99
,, cyanacetic, 861
,, cyanic, 116
,, ,, constitution of, 122
,, cyanilic, 123
,, cyanuric, 121
,, ,, constitution of, 122
,, damaluric, 962
,, decylic, or capric, 837
,, dehydracetic, 916
,, dehydrodihydroxybutyric, 906
,, dehydroglycolic, 883
,, dehydrolactic, 890
,, dehydromucic, 997
,, dehydrosarcolactic, 892
,, desoxalic, 953, 1012
,, dextrocamphoric, 975
,, dextronic, 585, 625, 903
,, dextrotartaric, 941
,, diallylacetic, 981
,, diaterebic, 950, 1012
,, diaterpenylic, 950
,, dibenzyldiparasulphonic, 362
,, dibromacetic, 860
,, dibromacrylic, 966
,, dibromhydrosorbic, 981
,, dibromobutyric, 864
,, dibromochlorobutyric, 864
,, dibromomaleic, 995
,, dibromopropionic, 466, 863
,, dichloracetic, 551, 859
,, dichloracrylic, 965
,, dichloropropionic, 862
,, dichloroxybutyric, 781
,, diconic, 980
,, dicyanic, 121
,, diethacetic, or secondary hexylic, 834
,, diethhydroxyacetic, or diethoxalic, 897
,, diethhydroxybutyric, 898
,, diethoxalic, 897
,, diethylmalonic, 933
,, digitalic, 694
,, diglycolamidic, 867
,, diglycolethylenic, 513
,, diglycolic, 513, 883
,, dihydracrylic, 885
,, dihydroxyacetic, or glyoxylic 899
,, dihydroxymalonic, or mesoxalic, 938
,, dihydroxypropionic, or glyceric, 902
,, dihydroxysuccinic, or tartaric, 941
,, diiodacetic, 861
,, diisoamylhydroxyacetic, 898
,, diisopropylhydroxyacetic, 898
,, dilactic, 890, *note*
,, dimethacetic, or isobutyric, 830
,, dimethacrylic, 958
,, dimethbromacetic, 864
,, dimethethacetic (tertiary hexylic), 834

Acid, dimethethoxyacetic, 896
,, dimethhydroxyacetic, 895
,, dimethiodacetic, 864
,, dimethoxalic, 895
,, dimethylmalonic, 931
,, α-dimethylsuccinic, 932
,, dimethyltartaric, 950
,, dinitroheptylic, 978
,, dinitroxysuccinic, 945
,, diphenylcarboxylic, 361
,, diphenyleneglycolic, 811
,, diphenylglycolic or benzilic, 787
,, ditartaric, 943
,, doeglic, 964
,, elaïdic, 963
,, erucic, 964
,, erythritic, 554
,, ethacetic, or butyric, 829
,, ethane-β-dicarboxylic, or isosuccinic, 930
,, ethylenecarboxylic, or acrylic, 955
,, ethylenelactic, or hydracrylic, 884
,, ethylcrotonic, 961
,, ethylhydroxybutyric, 897
,, ethylidenelactic, 887
,, ethylic or acetic, 824
,, ethylmalonic, 931
,, ethylnitrolic, 167, 168
,, ethylsuccinic, 932
,, ethylsulphonic, 708
,, formic, 821, 1011
,, frangulic, 694, 805
,, fulminuric (isocyanuric), 125, 177
,, fumaric, 967
,, ,, bromo-, 971
,, furfuracrylic, 767, 996
,, furfurangelic, 996
,, furfuropropionic, 996
,, furonic, 996
,, gluconic, 582, 903
,, glucovanillic, 692
,, glutaminic, 937
,, glutanic, 949
,, glutaric, 930
,, glyceric, or dihydroxypropionic, 902
,, glycinecarboxylic, 935
,, glycolic, 511, 585, 882
,, glycyrrhizic, 1009
,, glyoxylic, 899
,, halides, 853
,, heptylic, or œnanthylic, 834
,, hespertic, 696
,, hesperisic, 238
,, hexylhydroxyacetic, 898
,, hexylic or caproic isoprimary, 834
,, ,, ,, normal, 834
,, ,, ,, secondary, 834
,, ,, ,, tertiary, 834
,, hippuric, or benzamidacetic, 867
,, homovanillic, 685
,, hyænic, 839
,, hydracylic, 884
,, hydriodic, action of, 82
,, hydroauricyanic, 102
,, hydrobenzoic, 982

Acid, hydrobenzyluric, 982
,, hydrobromic, action of, 82
,, hydrochloric, action of, 82
,, hydrocobalticyanic, 112
,, hydrocyanic, 90, 1000
,, ,, conversion into formic acid, 93
,, ,, detection of, 94
,, ,, estimation of, 95
,, hydroferricyanic, 107
,, hydroferrocyanic, 104
,, hydrofuronic, 996
,, hydromeconic, 998
,, hydromuconic, 973
,, hydronitroprussic, 111
,, hydro-osmiocyanic, 113
,, hydro-oxycamphoronic, 978
,, hydroplatinibromocyanic, 114
,, hydroplatinocyanic, 114
,, hydrosorbic, 961
,, hydroxyacetic or glycolic, 882
,, hydroxyacetoformic, 906
,, hydroxybutyric, 895
,, hydroxycitraconic, 972
,, hydroxycitric, 955, 972
,, hydroxyformic, or carbonic, 876
,, hydroxyfumaric, 972
,, hydroxyisobutyric, 576, 895
,, hydroxyisosuccinic, or isomalic, 941
,, hydroxyitaconic, 972
,, hydroxymaleic, 972
,, hydroxymalonic or tartronic, 38
,, hydroxyparaconic, 973
,, hydroxypentylic, 896
,, α-hydroxypropionic, or hydracrylic 884
,, β-hydroxypropionic, or ethylidenelactic, 887
,, ,, inactive (lactic), 887
,, hydroxysuccinic or malic, 939
,, hydroxyvaleric, 896
,, hypogæic, 962
,, imides, 59
,, imidocaprylic, 811
,, iodides, 59
,, iodobutyric, 864
,, ipomæic (sebacic), 693, 934
,, isoamyl, 897
,, isoamylhydroxyacetic, 897
,, isobutyric, 830
,, isocrotonic, 957
,, isocyanuric (fulminuric), 125
,, isomalic, or hydroxyisosuccinic, 941
,, isophloretic, 699
,, isopropacetic (isoprimary valeric), 447 831
,, isoprophydroxyacetic, 896
,, isopropylacrylic or pyroterebic, 950, 961
,, isopyromucic, 996
,, isosuccinic, or methylmalonic, 930
,, ,, monobromo-, 935
,, isotrichloroglyceric, 903
,, itachloropyrotartaric, 935

Acid, itaconic, 969
,, itamalic, 949
,, itatartaric, 949
,, jalapic, 697
,, α-jalapic, 697
,, jalapinolic, 697
,, lactic, 581, 736, 887
,, ,, etheric acids derived from, 889
,, lævocamphoric, 975
,, lævotartaric, 943
,, lævulinic, 603, 917
,, lauric, 838
,, lepargylic or anchoic, 933
,, leucic, 896
,, linoleic, 962
,, maleic, 968
,, ,, bromo-, 971
,, ,, chloro-, 972
,, malic or hydroxysuccinic, 939, 1012
,, malonic, 925, 1012
,, ,, dibromo-, 934
,, mandelic, 688, 757
,, mannitic, 558, 903
,, margaric, 838
,, meconic, 998
,, melissic, 840
,, mesachloropyrotartaric, 935
,, mesaconic, 969
,, mesocamphoric, 975
,, mesoxalic or dihydroxymalonic, 938
,, mesotartaric, 948
,, metacetonic (propionic), 828
,, metatartaric, 943
,, methanedicarboxylic or malonic, 925
,, methacetic (propionic), 828
,, methacetylenecarboxylic or tetrolic, 980
,, methacrylic, 958
,, ,, bromo-, 966
,, ,, chloro-, 966
,, methethacetic (secondary valeric), 447, 831
,, methethhydroxyacetic, 896
,, methethhydroxybutyric, 898
,, methethoxalic, 896
,, methhexacetic (nonylic), 836
,, methhydroxyphthalic, 675
,, methydroxyacetic, or ethylidenelactic, 887
,, methhydroxybutyric, 896
,, methylcrotonic, or tiglic, 958
,, methylethacrylic, 961
,, methylic (formic), 821
,, methylmalonic, or isosuccinic, 930
,, methylpropane-α-dicarboxylic, 932
,, methylsuccinic, or pyrotartaric, 931
,, moniodacetic, 861
,, moniodopropionic, 861
,, monobromacetic, 860
,, α-monobromopropionic, 861
,, β-monobromopropionic, 862
,, monochloracetic, 859
,, monochlorobutyric, 863
,, α-monochloropropionic, 861
,, β-monochloropropionic, 861
,, mononitroheptylic, 978

Acid, moringic, 962
,, mucic, 587, 611, 951
,, mucobromic, 995
,, mucochloric, 995
,, muconic, 973
,, myristic, 238
,, myronic, 697
,, naphthalic, 358
,, nitric, action of, 82
,, nitrococcusic, 690
,, nitropyromeconic, 999
,, β-nitrosopropionic, 915
,, nitrous, action of, 82
,, β-nitroxypropionic, 889
,, nonylic, or pelargonic, normal, 836
,, ,, ,, isoprimary, 836
,, octylic, or caprylic, normal, 835
,, ,, ,, isosecondary, 835
,, œnanthylic, or heptylic, 834
,, oleic, 962
,, orsellinic, 528
,, orthocarbonic, 877
,, orthobenzoylbenzoic, 386
,, orthoformic, 823
,, oxalic, 920
,, oxyacetic, or glycolic, 882
,, oxybutyric, or hydroxybutyric, 895
,, oxycamphoronic, 978
,, oxisobutyric, or hydroxyisobutyric, 516, 895
,, oxypicric (trinitroresorcinol), 523
,, oxypyromecazonic, 999
,, oxytetric, 981
,, oxyvaleric, 516
,, palmitic, 838
,, palmitolic, 981
,, parabenzoylbenzoic, 385
,, paracamphoric, 975
,, paraconic, 973
,, paradipimalic, 885
,, paraffinic, 144
,, paralactic, 891
,, paramethoxyphenylacrylic, 764
,, paraphenylbenzoic, 385
,, pelargonic, or nonylic, normal, 836
,, ,, ,, isoprimary, 836
,, pentane-α-dicarboxylic, 933
,, pentic, 981
,, pentylic (valeric), 830
,, phoronic, 978
,, persulphocyanic, 120
,, phenoldisulphonic, 479
,, phenolmetasulphonic, 479
,, phenolorthosulphonic, 478
,, phenolparasulphonic, 478
,, phenolpropionic, 493
,, phenoltrisulphonic, 479
,, phloretic, 699.
,, picramic (amidodinitrophenol), 478
,, picric (trinitrophenol), 476
,, pimelic, 932, 933
,, pivalic, 783
,, propacetic (normal valeric), 830
,, propane-α-dicarboxylic, or glutaric, 930

Acid, propanetricarboxylic, or tricarballylic, 952
,, propionic, 828
,, propylacrylic (hydrosorbic), 961
,, propylnitrolic, 168
,, prussic (hydrocyanic), 90
,, pyromeconic, 999
,, pyromucic, 766, 993
,, ,, tetrabromide, 994
,, β-pyromucic, 767, 996
,, pyroracemic, or pyruvic, 904
,, pyrotartaric, 931
,, ,, itachloro-, 935
,, ,, mesachloro-, 935
,, pyroterebic, 950, 961
,, pyruvic, or pyroracemic, 904
,, quartenylic, or isocrotonic, 957
,, quinovatannic, 699
,, quinovic, 699
,, racemic, 946
,, ratanhia-tannic, 700
,, ricinoleic, 917
,, rocellic, 934
,, rosolic, 763
,, ruberythric, 802, *note*
,, rubiacic, 802, *note*
,, rufigallic, 807
,, rutic, or capric, 837
,, saccharic, 950
,, salicylic, 930
,, salicylous (salicylic aldehyde), 760
,, sarcolactic, 891
,, ,, optical activity of, 892
,, scammonic, 697
,, Scheele's (hydrocyanic), 93
,, sebacic, or sebic, 934
,, sorbic, 981
,, stearic, 839
,, stearolic, 982
,, stearoxylic, 982
,, styphnic (trinitroresorcinol), 523
,, suberic, 933
,, succinic, 925
,, ,, dibromo-, 934
,, ,, monobromo-, 934
,, ,, tribromo-, 934
,, sulphocamphoric, 975
,, sulphocarbonic, or thiocarbonic, 880
,, sulphocyanic, 120
,, tampicic, 703
,, tampicolic, 703
,, tannic (tannin), 703
,, tartaric, 941
,, tartrelic, 943
,, tartronic, 938
,, teracrylic, 962
,, terebic, 238, 950
,, terpenylic, 238, 950
,, tetrahydrobenzoic, or benzoleic, 982
,, tetrahydroxytetranedicarboxylic (saccharic), 950
,, tetramethylsuccinic, 933
,, tetraneglycinecarboxylic (glutaminic), 937
,, tetric, 981

Acid, tetrolic, 980
,, tetrylacetic, or caproic isoprimary, 834
,, ,, ,, normal, 833
,, tetrylic (butyric), 829
,, thiacetic, 851
,, thiocarbonic, 880
,, thiodiglycolic, 884
,, thioglycolic, 884
,, thujetic, 703
,, tiglic, 958
,, tribromacetic, 860
,, tribromolactic, 893
,, tricarballylic, 952
,, trichloracetic, 513, 859
,, trichloracetonic, 782
,, trichlorhydroxyvaleric, 896
,, trichlorobutyric, 516, 864
,, trichlorolactic, 744, 893
,, trigenic, 736
,, triglycolamidic, 867
,, trihydrocyanic, 94
,, trihydroxybutyric, 903
,, trimethacetic (tertiary valeric), 447, 783, 832
,, trinitrocresotic, 690
,, turpethic, 704
,, turpetholic, 704
,, urochloralic, 514
,, valeric, isoprimary, 831
,, ,, primary, 830
,, ,, secondary, 831
,, ,, tertiary, 832
,, vanillic, 684, 685
,, veratric, 682
,, xanthic, 880
,, xeronic, 974
Acidhydrols, 823
Acids, acetic, series of, 820
,, ,, ,, haloid derivatives of, 857
,, ,, ,, hydroxyl derivatives of, 871
,, acrylic, series of, 953
,, amido-, 864
,, bromacetic, 860
,, camphoric, 974
,, caproic, 833
,, carbo-, 56
,, carboxylic, 56
,, chloracetic, 858
,, definition of, 816
,, ethanedicarboxylic, 925
,, etheric, derived from lactic acid, 889
,, general properties of, 818
,, glycolic, or lactic series of, 873
,, haloid derivatives of, 60
,, hexanedicarboxylic, 933
,, hexylic, or caproic, 833
,, hydroxyadipic, 949
,, hydroxybutyric, 894
,, hydroxycaproic, 896
,, hydroxydodecylic, 898
,, hydroxyheptylic, 897
,, hydroxyoctylic, 898
,, hydroxypropane-α-dicarboxylic, 949
,, hydroxypyrotartaric, 949

Acids, hydroxyvaleric, 896
,, iodacetic, 861
,, ketonic, 904
,, lactic, 884
,, maleic, series of, 967
,, malic (isomeric), 941
,, modes of formation, 817
,, nitrolic, 167
,, organic, 56
,, pentanecarboxylic, 932
,, phosphonic, 57
,, propanedicarboxylic, 930
,, pyrocitric, 969
,, succinic series of, 918
,, sulphuric, 57
,, sulpho-, 57
,, sulphonic, 57
,, tetranedicarboxylic, 932
,, thiocarbonic, 880
,, valeric, series of, 830
Acraldehyde, or acrolein, 545, 752
Acrinyl thiocyanate, 702
Acroleïn, or acraldehyde, 545, 752
Acrothialdin, 754
Acrylates, 956
Action of halogens on carbon compounds, 78
Æscigenin, 688
Æsorceïn, 687
Æscorcin, 688
Æsculetin, 687
,, par-, 687
,, trianil-, 687
,, triacetyl-, 687
Æsculin, 687
,, hexacetyl-, 687
,, trianil-, 687
Agents, dehydrating, action of, 83
,, oxydizing, action of, 71
,, reducing, action of, 75
Ajowan, oil of, 242
Alanine, or propane-glycine, 738, 868
β-alanine-α-carbonamide, 936
Alban, 246
Alcohol (ethylic alcohol), 425, 1005
,, absolute, 426
,, allylic, 464
,, amidoethylic (aldehyde-ammonia), 737, 1010
,, amylic, higher homologues of, 457
,, ,, isoprimary, 445
,, ,, normal primary, 445
,, ,, tertiary, 450
,, benzylic, 490
,, bromopropylic, 515
,, butylic, normal primary, 438
,, ,, isoprimary, 438
,, ,, secondary, 439
,, ,, tertiary, 439
,, cerylic, 457
,, cetylic, 457
,, α-chloropropylic, 514
,, cinnamic, 495
,, coniferylic, 691
,, cumic, 494
Alcohol, cuminylic, 494
,, cyanethylic, 736
,, decylic, 457
,, diacetonic, 780
,, dichlorisopropylic, 541
,, dichloropropylic, 541
,, diglyceric, 546
,, ethylenic, 509
,, ethylic, 425, 1005
,, ,, higher homologues of, 457
,, fluorene, 503
,, furfurylic, 766
,, heptylic, normal primary, 454
,, ,, isoprimary, 454
,, ,, secondary, 455
,, ,, tertiary, 455
,, hexylic, normal primary, 452
,, ,, isoprimary, 452
,, ,, secondary, 452
,, ,, tertiary, 452
,, iodopropylic, 515
,, isopropylic, 435
,, melissic, 457
,, menthylic, 467
,, methylic, 422, 1005
,, mononitrobenzylic, 490
,, naphthalenic, 554
,, octylic, or caprylic, primary, 456
,, paratolylic, 492
,, paroxybenzylic, 763
,, phenylethylic, primary, 492
,, ,, secondary, 492
,, phenylpropylic, primary, 494
,, ,, secondary, 494
,, piperonylic, 765
,, propargylic, 467
,, propylic chloro-, 191
,, ,, primary, 434
,, ,, secondary, 435
,, sycocerylic, 495
,, thioallylic, 662
,, thioamylic, 662
,, thiobenzylic, 662
,, thiobutyric, 662
,, thioethylic, 661
,, thioisobutylic, 662
,, thioisopropylic, 661
,, thiomethylic, 661
,, thiopropylic, 661
,, triglyceric, 546
,, vanillylic, 765
,, vinylic, 213
Alcohols, 53, 403
,, allylic, series of, 464
,, amylic, 444, 1005
,, ,, secondary, 449
,, benzene series of, 469
,, benzylic series of, 468, 471
,, butylic, 438
,, dihydric, 504
,, ether-, 682
,, ethylic series of, 404
,, ,, ,, classification of, 405
,, ,, ,, diagnoses of, 415, 1004

Alcohols, ethylic series, of formation of, 407
,, ,, ,, haloid derivatives of, 461
,, ,, ,, isomerism of, 406
,, ,, ,, properties of, 415–422
,, general characters of, 403
,, ,, review of, 563
,, heptylic, 454, 562, 1005
,, hexylic, 452
,, nonylic, 457
,, octylic, 456
,, pentylic, 444
,, polyglyceric, 546
,, primary, 405, 407, 416
,, propylic, 434
,, secondary, 405, 410, 416
,, tertiary, 405, 411, 417
,, thio- (mercaptans), 659
,, tritylic (propylic), 434
Aldehyde, acetic or ethylic, 727 (*see* Ethaldehyde)
,, acrylic (acroleïn), 545, 752
,, ammonia, 737
,, ,, compounds of, 737
,, amylic, 750
,, anisic, 763
,, benzoic, 755 (*see* Benzaldehyde)
,, ,, homologues of, 1010
,, butyric, 748
,, caproic (hexaldehyde), 751
,, cetylic, 751
,, chlorobutyric, 754
,, cinnamic, 241, 767
,, crotonic, 754
,, cumic or cuminic, 241, 766
,, dipheneth-, 1006
,, ethylic or acetic, 727 (*see* Ethaldehyde)
,, formic, 723
,, isobutyric, 749
,, isovaleric, 750
,, methyleneprotocatechuic, 765
,, methylic, 723
,, methylprotocatechuic, 764
,, naphthoic, 768
,, œnanthylic (œnanthol or heptaldehyde), 751, 1010
,, oxalic (glyoxal), 768
,, oxybutyric, 733, 748
,, palmitic, 751
,, parametadioxybenzoic, 764
,, parametamethylenoxybenzoic, 765
,, paramethoxybenzoic or anisic, 763
,, paramethylbenzoic, 765
,, paratoluic, 765
,, parethoxymetamethoxybenzoic, 764
,, paroxybenzoic, 763
,, paroxymetamethoxybenzoic, 692, 764
,, pheneth-, 1010
Aldehyde, phenylacetic, 765
,, phenylacrylic, 767
,, phthalic, 770, 1010
,, piperonylic, 765
,, propionic or propylic, 747
,, protocatechuic, 764, 1010
,, α-pyromucic, 766, 1010
,, β-pyromucic, 767
,, -resin, 731
,, salicylic, 760
,, succinic, 770
,, terephthalic, 770
,, toluic, 765
,, trichlorobutyric, 749
,, valeric, 750
Aldehydes, 55, 714
,, aromatic, 755
,, formation of, 715
,, general properties of, 716
,, pent-, 750
,, table of, 722, 755
Aldehydin, 737
Aldehydrols, 504
Aldines, 721
Aldol, 733, 748
,, polymerides of, 748
Ale, 433
Alizarin, 802
,, amido-, 804
,, brom-, 804
,, constitution of, 376
,, diacetyl-, 804
,, isomerides of, 804, 1011
,, manufacture of, 803
,, methyl-, 807
,, nitro-, 804
Alkalis, action of, 85
Allene, 218
Allylacetone, 789
Allylbenzene, 342
Allyldimethylcarbinol, 466, 1005
Allylene, 217
,, iso-, 218
,, moniod-, 468
,, monobrom-, 468
,, monochlor-, 468
Allylenic dibromide, 206
,, oxide, 218
,, tetrachloride, 159
Allylic acrylate, 957
,, bromide, 205, 206
,, brom-, acetate, 206
,, ,, nitrate, 206
,, ,, thiocyanate, 206
,, chloride, 203
,, formate, 847
,, iodide, 207, 544
,, mercur-, iodide, 207
,, sulphide, 711
,, tribromide, 160
,, tricyanide, 175
,, trioxide, 679
Aloïn, 808
Aloxanthin, 808
Aluminic acetate, 827

Amarine, 757
Amic acids, 59
Amides, acid, 59
Amidin (starch), 616
Amidon (starch), 616
Amines, 61
Ammonia type examples of, 69
Ammonic acetate, 826
,, adipate, 932
,, carbamate, 879
,, cyanate, 118
,, malate, 940
,, sulphocyanate, 120
,, thiocarbonates, 881
Amygdalin, 688
,, heptacetyl-, 688
Amylaceous group, 616
Amylacetylene, (œnanthylidene), 221
Amylcarbinol, 455
Amyldimethylbenzene, 296
Amylene, 193, 448 (*note*), 825 (*note*), 1001.
,, dibrom-, 220
Amylenic chloride, 162
,, hydrate, 450
,, oxide, 679
Amylic chloride, 162
,, hydride, 139
,, iodide, 193
Amylin, or dextrin, 627, 1009
Amylmethyl, 139
Amylmethylbenzene, 296
Amylodextrin, 634
Amylon, or starch sugar, 612, 626, 1008
Amylum (starch), 616
Analysis, calculation of, 35
,, of bodies containing nitrogen, 22
,, of carbon compounds, 3
,, of gaseous mixtures, 32
,, of liquids, 21
,, proximate, 3
,, ultimate, 4, 11, 13, 1000
Anethol, 241, 675, 1009
Angelates, 960
Anhydride, abietic, 239
,, acetic, 855
,, amidocamphoric, 977
,, bromocitraconic, 972
,, camphoric, 976
,, ,, bromo-, 976
,, citraconic, 969, *note*
,, chlorocitraconic, 972
,, diacetotartaric, 945
,, diacetoxysuccinic, 945
,, glutaric, 931
,, hydroxycamphoric, 976
,, maleic, 969
,, methylsuccinic, 931
,, pyrotartaric, 931
,, succinic, 947
,, sulphocyanic, 120
,, tartaric, 943
,, thiacetic, 856
,, trimethacetic, 856
,, xeronic, 974
Anhydrides, acid, 60
Animal oil, Dippel's, 258
Anise, oil of, 241
Anisol, 674
Anisylic hydride, 763
Anol, 496
Anthracene, 370
,, constitution of, 374, 1004
,, dibrom-, 374
,, ,, tetrabromide, 374
,, dichloro-, 374
,, dichloride, 373
,, dihydro-, 367, 373
,, dioxy-, 536
,, hexahydro-, 355, 373
,, methyl-, 382
,, monobrom-, 374
,, monochlor-, 373
,, tetrabrom-, 374
,, tetrachlor-, 374
,, tetroxy-, 803
,, tribrom-, 374
Anthrachrysone, 807
Anthraflavone, 805, 1011
Anthragallol, 807
Anthrahydroquinone, or anthraquinol, 536, 1007
Anthranol, 1006
Anthraquinone, 801
,, constitution of, and its derivatives, 374, 809, 1011
,, dibrom-, 801
,, dichlor-, 801
,, dimethyl-, 807
,, dinitro-, 801
,, dioxy-, derivatives of, 802 *et seq.* (*see* also Alizarin)
,, erythroxy-, 802
,, hexoxy-, 807
,, methyl-, 807
,, monobrom-, 801
,, monoxy-, 802
,, sulphonic, acids of, 801
,, tetroxy-, 807
,, trioxy-, derivatives of, 805 *et seq.*
Anthrarufin, 1011
Anthrols, 504, 1006
Aphrodescin, 688
Apigenin, 688
Apiin, 688
Arabin, 589, 651
Arabinose, 589, 654
Arbutin, 689
,, di-, 689
,, tetranitro-, 689
Argentallylene, 218
Argentic acetate, 826
,, acetoformate, 905
,, acrylate, 956
,, angelate, 960
,, butyrate, 830
,, crotonate, 957
,, cyanide, 99
,, cyanurates, 122
,, dimethacrylate, 960

Argentic dimethethacetate, 83
,, formate, 823
,, fulminate, 123
,, furonate, 996
,, heptylate, 835
,, hydracrylate, or α-hydroxypropionate, 886
,, isobutyrate, 830
,, isovalerate, 831
,, meconate, 998
,, methethacetate, 832
,, nonylate, 836
,, potassic fulminate, 124
,, propionate, 828
,, pyruvate, or acetoformate, 905
,, trimethacetate, 833
Argol, 942
Arnicin, 690
Arrack, 432
Arrowroot, 622
Arsenicum, in carbon compounds, determination of, 26
Artiads, 47
Asparagine, 986
Asphalt, 146
Asymmetric carbon atom hypothesis, 986
Atom, distinguished from molecule, 42
Aurantin, 690
Aurous cyanide, 101
Austracamphene, 235
Austraterebenthene, 234
Avogadro's law, 38

BALSAM of Canada, 239
Barbaloïn, 808
Baric acetate, 826
,, angelate, 960
,, caprate (rutate), 838
,, caproate, 834
,, cobalticyanide, 112
,, dimethacrylate, 960
,, dimethethacetate, 834
,, dimethoxalate, 895
,, heptylate, 835
,, isocaproate, 834
,, isovalerate, 831
,, methethacetate, 832
,, nitroprusside, 111
,, nonylate, 836
,, octylate, 835
,, oleate, 964
,, pelargonate, 836
,, propionate, 828
,, pyromeconate, 999
,, trimethacetate, 833
,, valerate, 831
Barley sugar, 597
Barras (galipot), 226
Bay, oil of, 241
Beer, 433
Benylene, 222
Benzaldehyde, 755
,, dichloro-, 760
,, haloid derivatives of, 759
,, homologues of, 765
Benzaldehyde, metanitro-, 760
,, nitro-derivatives of, 760
,, orthochloro-, 760
,, orthomethoxy-, 761
,, orthoxy- (salicylol), 760
,, parachloro-, 760
,, thio-, 759
,, trichloro-, 760
Benzene, 258, 1003
,, action of re-agents on, 1004
,, allyl-, 342
,, amyl-, 295
,, amyldimethyl-, 296
,, amylmethyl-, 296
,, benzyl- (diphenylmethane), 360
,, bromiodo-, 311
,, bromo-, 300
,, bromonitramido-, 333
,, bromotrimethyl-, 321
,, β-butyl-, 288
,, chloriodo-, 311
,, chloro-, 305, 1004
,, chlorobromo-, 311
,, chloromethyl-, 313
,, chloromethylchloro-, 314
,, chloromethydichloro-, 315
,, chloromethylpentachloro-, 317
,, chloromethyltetrachloro-, 316
,, constitution of, 261, 270, 338, 817, *note*
,, cyano-, 327
,, derivatives, constitution of, 264
,, diacetenyl-, 385
,, dibenzyl-, 385
,, dibromo-, 300
,, dichloro-, 307
,, dichloromethyl-, 314
,, dichloromethylchloro-, 315
,, dichloromethyldichloro-, 316
,, dichloromethylpentachloro-, 317
,, dichloromethyltetrachloro-, 317
,, dichloromethyltrichloro-, 316
,, dichlorotetroxy-, 796
,, diethyl-, 293
,, diethylmethyl-, 296
,, diiodo-, 311
,, dimethyl-, 285
,, dinitro-, 324
,, ethyl-, 284
,, ethylbromo-, 321
,, ethyldimethyl-, 294
,, ethylmethyl-, 286
,, ethylnitro-, 326
,, fluor-, 310
,, haloid derivatives of, 298
,, hexabromide, 300
,, hexachloride, 305
,, hexabromo-, 1004
,, hexachloro-, 309
,, hexyl-, 296
,, homologues of, 276, 1003
,, ,, action of hydrogen on, 281
,, ,, action of halogens on, 281

Benzene, homologues of, oxidation of, 279
,, iodo-, 310, 1004
,, isocyano-, 328
,, isopropyl-, 286, 1003
,, metabromiodo-, 311
,, metadichloro-, 308
,, metadibromo-, 301
,, metadicyano-, 329
,, metadiiodo-, 311
,, metadimethylbromo-, 321
,, metadimethyldibromo-, 321
,, metadioxy-, 521
,, metanitrocyano-, 328
,, metatribromo-, 306
,, methyl-, 283 (*see* Toluene)
,, methylchloro-, 313
,, methyldichloro-, 314
,, methyldipropyl-, 297
,, methylpentachloro-, 316
,, methyltetrachloro-, 316
,, methyltrichloro-, 315
,, nitro-, 323
,, ,, dihaloid derivatives of, 331
,, ,, monohaloid derivatives of, 330
,, ,, trihaloid derivatives of, 331
,, nitrodichloramido-, 333
,, nitroparadimethyl-, 325
,, orthochloriodo-, 311
,, orthodibromo-, 302
,, orthodichloro-, 308
,, orthodiethyl-, 293
,, orthodiiodo-, 311
,, orthodinitro-, 324
,, orthodioxy-, 524
,, orthotribromo-, 304
,, oxydimethyl- (xenol), 492
,, oxyethyl-, 493
,, parabromiodo-, 311
,, parachloriodo-, 311
,, parachlorobromo-, 311
,, paradibromo-, 300
,, paradichloro-, 307
,, paradicyano-, 329
,, paradiethyl-, 293
,, paradinitro-, 324
,, paradimethoxy-, 533
,, paradimethylbromo-, 321
,, paradioxy-, 525
,, paradiphenyl-, 385
,, parapropylmethyl-, 289
,, paratribromo-, 302
,, paratrichloro-, 309
,, pentabromo-, 305
,, pentachloro-, 309
,, properties of, 259
,, propyl-, 286
,, propyldimethyl-, 296
,, propylisopropyl-, 1003
,, propylmethyl-, 289
,, symbol, Kekulé's, 338
,, table of homologues of, 278
,, tetrabromo-, 305
Benzene, tetrachloro-, 309
,, tetrachlorodioxy-, 796
,, tetramethyl-, 294
,, tribromo-, 302
,, trichloro-, 309
,, trichloromethyl-, 315
,, trichloromethylchloro-, 316
,, trichloromethyldichloro-, 316
,, trichloromethyltetrachloro-, 317
,, trichloromethyltrichloro-, 317
,, triethyl-, 296
,, triiodo-, 311
,, trimethyl-, 289
,, trinitro-, 1004
,, triphenyl-, 390
Benzhydrol, 503, 786
Benzil (dibenzoyl), 787
Benzimide, 758
Benzohelicin, 695, 699
Benzoin (benzoylphenylcarbinol), 787
Benzonitrile, 327
Benzopinacone, 786
Benzoyl hydride, 755
Benzoylphenylcarbinol (benzoin), 787
Benzylbenzene, or diphenylmethane, 360
Benzylethylbenzene, 363
Benzylic or benzoic alcohol, 490
,, bromide, 319
,, chloride, 313
,, oxalate, 923
,, selenide, 713
,, sulphide, 712
,, sulphydrate, 662
,, telluride, 714
Benzylmetaxylene, 363
Benzylnaphthalene, 383
Benzylparaxylene, 363
Benzylphenyl, 503
Benzyltoluene, ortho-, 362
,, para-, 362
,, tetranitro-, 363
Bergamot, oil of, 240
Betaorcin, 533
Benzoic chloride, action of, 86
Bitter almond oil, 755
Bitumen, 146
Bonds, 44
Bone oil, 258
Bones, destructive distillation of, 258
Bornenee, 240
Borneo camphene, 233
Borneo camphor or borneol, 791
Borneol, 791
Bornesite, 562
Brandy, 432
British gum, 623
Bromacetic bromides, 860
Bromal, 747
Bromalide, 894
Bromallylic acetate, 206
,, nitrate, 206
,, thiocyanate, 206
Bromhydranil, 526
Bromhydrins, 54, 463
Bromine acetate, 850

Bromine, determination of, in carbon compounds, 28
Bromobutylene bromide, 162
Bromoform, 153
Bromopicrin, or tribromonitromethane, 170
Bromoxaform (pentabromacetone), 782
Bryonin, 690
Bryoretin, 690
Bunsen's method for combustions, 18
Butaldehyde, 747
Butane, haloid derivatives of, 161
,, dibromo-, 161
,, iso-, 138
,, moniodo-, 161
,, monobromo-, 161
,, monochloro-, 161
,, normal, 138
,, tetrabromo-, 162, 219
,, tribromo-, 162
Butanes, 138
Butene, 191
Butylcarbinol, 445
,, secondary, 445
Butyldimethylcarbinol, tertiary, 455
Butylene, or tetrylene, 191
,, dichloro-, 754
,, normal, 191
,, α-phenyl-, 342
,, β-phenyl-, 343
Butylenic bromides, 161
Butylethylene, 195, 196
Butylic aldehyde, 747
,, bromides, 161
,, chlorides, 161
,, hydride, 138
,, iodides, 161
Butylmethyl, 139
Butylmethylcarbinol, primary, 452
,, secondary, 453
Butyric aldehyde, 747
,, ,, chloro-, 754
,, peroxide, 856

CAINCIGENIN, 690
Caincin, 690
Cajeputol, 467
Calamus, oil of, 297
Calcic acetate, 826
,, adipate, 932
,, angelate, 960
,, butyrate, 829
,, caproate, 833
,, carbamate, 879
,, citrate, 952
,, dihydroxyacetate, or glyoxalate, 901
,, dimethacrylate, 960
,, glycolate, or hydroxyacetate, 883
,, glyoxylate, 901
,, heptylate, 835
,, hydracrylate, or α-hydroxypropionate, 887
,, isobutyrate, 830
,, isocaproate, 834
,, lactate, 889
,, malate, 940
Calcic octylate, 835
,, pimelate, 933
,, propionate, 828
,, succinate, 927
,, tartrate, 945
,, trimethacetate, 833
,, valerate, 831
,, xeronate, 974
Calculation of analyses, 35
Camphenes, 232
,, Austra-, 235
,, Borneo-, 233
,, tere-, 232
Campholene, 977
Camphor, 790, 1010
,, Borneo, 791
,, constitution of, 792
,, from camphene, 237
,, ,, feverfew oil, 790
,, laurel, 790
,, monobromo-, 792
,, monochloro-, 792
,, oil, 240
,, sodium-, 790
Camphoric peroxide, 237
Canada balsam, 239
Cannel coal, destructive distillation of, 254
Cane sugar (saccharon), 593, 1008
Caoutchin, 244
Caoutchouc, 243
Caprylidene, 221
Caramel, 598
Caraway, oil of, 241
Carbamines, properties of, 174
,, table of, 173
Carbinols, 405
,, diagnosis of, 1004
,, tertiary, 1004
Carbo-acids, 56
Carbohydrates, 567
,, constitution of, 654
,, nomenclature of, 659.
,, reducing power of, 568, 1007
,, specific rotatory power of, 569
,, synthesis of, 1008
Carbon dichloride, 201
Carbonates, 876
Carbonic tetrabromide, 154
,, tetrachloride, 153
,, tetriodide, 151
Carbonyl-dibiuret, 122
Carbothialdine, 739
Carboxylic acids, 56
Carburetted hydrogen, light (methane), 133
,, ,, heavy (ethylene), 183
Carius's method for determining chlorine, bromine, and iodine, 28
Carmine-red, 690
Carpene, 224
Carvacrol, 494
Carvene, 241
Carvol, 241

Cassia, oil of, 241
Catechol, or pyrocatechin, 524
,, dimethyl, 682
,, methyl-, 532
,, monethylin-, 683
Cedriret, or cœrulignone, 800, 1010
Cellulose, 645
,, estimation of, 646
,, hydro-, 650
,, nitro-, 649
,, soluble in ammoniacal oxide of copper, 647
Cerotene, 199
Cetene, or cetylene, 199
Cetenylene, 222
Cetine, 222
Cetylene, or cetene, 199
,, dibromide, 222
Cetylic bromide, 163
,, chloride, 163
,, iodide, 163
Change of valency, 47
Chapeau (of must), 433
Chemical types, 67
Chemistry, inorganic, 1
,, organic, 1, 49
,, physiological, 2
Chinese yellow, 700
Chinizarin, 804
,, constitution of, 376
Chloracetic chlorides, 859
Chloracetin, 676
Chloral, 743
,, alcoholate, 683
,, ammonia, 745
,, hydrate, 513, 744
,, meta-, 743
Chloralide, 744
,, and analogous compounds, 893
,, glycolic, 894
,, lactic, 894
Chloranil, or tetrachlorquinone, 795
Chlorethylic acetate, 736
Chlorhydrinimide, 542
Chlorhydrins, 54, 463
Chlorine acetate, 849
,, iodine and bromine, determination of, in carbon compounds, 28
Chlorhydranil, 526
Chloroform, 151
Chloropicrin, 170
Chloropropylenic oxide (epichlorhydrin), 542
Cholesterin, 496, 1006
Chrysazin, 805, 1006, 1011
,, oxy-, 807
Chrysene, 386
,, dibromo-, 387
,, dichloro-, 387
,, dinitro-, 387
,, mononitro-, 387
,, series of hydrocarbons, 386
,, tetranitro-, 387
Chrysenehydroquinone or chrysoquinol, 537, 812
Chrysoquinone, 387, 812
Chrysorhamnin, 700
Cider, 433
Cinnamene, 340
,, bromo-, 341
,, chloro-, 341
,, dibromide, 341
,, meta-, 342
,, nitro-, 342
,, series of hydrocarbons, 340, 1004
Cinnamon, oil of, 241
Cinnamol (cinnamene), 340
Cinnamic chloride, 342
,, cyanide, 342
,, iodide, 342
Citronellol, 467
Classification of carbon compounds, 49
Cloves, oil of, 297
Coal, destructive distillation of, 247
,, cannel-, destructive distillation of, 254
,, -gas, manufacture of, 248
,, -naphtha, 247, 252
,, -tar, 247
,, compounds present in, 251, 1003
,, distillation of, 252
Cobalticyanides, 111
Cobaltocyanides, 111
Coccinin, 691
Cochineal, 690
Cœrulignone, or cedriret, 800
Coke, gas-, 247
Collidine, 738
Collodion, 647
Colocynthein, 691
Colocynthin, 691
Colocynthitin, 691
Colophene, 229, 232
Colophony, 239
Combination, direct, 43
,, often double decomposition, 42
Combustion, Bunsen's method, 18
,, Dumas's method, 19
,, furnace, 13
,, tube, 15
,, ,, filling, 17
,, with plumbic chromate, 20
Common frankincense, 226
Compound radicles, theory of, 64
Compounds, organo-metallic, 63
,, saturated, 50
,, unsaturated, 50
Concretor, Fryer's, 594
Coniferin, 691
Constitution of anthracene, 374, 1004
,, of anthraquinone, 374, 809, 1011
,, of naphthalene, 346
,, of phenol derivatives, 485
Convallarin, 692
Convallamaretin, 692
Convallamarin, 692
Convolvulin, 692
Convolvulinol, 692
Coriander, oil of, 241
Cork, 645

Coumarin, 762
Creasote, 255
Creosol, 684
Cresol, 491
,, nitro-, 491
Crocetin, 693
Crocin, 693
Crotonaldehyde, 754
Crotonylene, 218
Crystallization, fractional, 6
Cubebs, oil of, 297
Cumene, from cumic acid (isopropylbenzene), 286
,, pseudo- (from coal tar), 288
Cumin, oil of, 241
Cuminol (cumic aldehyd), 766, 1003
Cupric acetates, 827
,, cyanide, 99
,, formate, 823
,, glycolate or hydroxyacetate, 883
Cuprosoacetylic chloride, 214
,, oxide, 214
Cuproso-cupric cyanide, 99
Cuproso-vinylic ether, 214
Cuprous acetylide, 214
,, cyanide, 99
,, sulphocyanate, 119
Cuticular substance, 645
Cyamelide, 117, 122
Cyanethine, 174
Cyanic bromide, 116
,, chloride, 115
,, iodide, 116
,, sulphide, 120
Cyanides, 96
,, detection of, 94
,, double, 98
Cyanmethine, 174
Cyano-derivatives of benzene, 327
,, ,, the homologues of benzene, 329
,, ,, the hydrocarbons, 52
Cyanoform, 175, 1001
Cyanogen acetate, 850
,, bromides, 116
,, chlorides, 115
,, conversion of into ammonic oxalate, 89
,, formation of, 88
,, iodide, 116
,, liquefaction of, 89
,, preparation of, 88
,, solubility in water, 88
,, sulphide, 120
Cyanuric bromide, 116
,, chloride, 116
Cyaphenine, 328
Cyclamin, 693
Cyclamiretin, 693
Cymene, 289, 1003
,, dihydrides, 291
,, mononitro-, 326
Cymoquinone, 798
,, dioxy-, 799
,, oxy-, 799

DAMBONITE, 562
Dambose, 561
Daphnetin, 693
Daphnin, 693
Datiscetin, 693
Datiscin, 693
Dead oil (from tar), 252
Decane, dibromo-, 198
,, normal, 141
Decanes, 141
Decenylene, 221
Decylene or decene, 197
Dehydrating agents, action of, 83
Dehydrotriacetonamine, 780
Deoxybenzoin, 787
Desiccation of organic compounds, 11
Destructive distillation of bones, 258
,, ,, cannel coal, 254
,, ,, coal, 247
,, ,, lignite, 254
,, ,, menhaden oil-soap, 257
,, ,, peat, 257
,, ,, wood, 254
Determination of carbon and hydrogen, 12, 21
,, ,, nitrogen, 22
,, ,, sulphur, phosphorus and arsenic, 26
,, ,, haloids, 28
,, ,, vapour densities, 36
Dextrin or amylin, 627
Dextroglucose, or dextrose, 577
,, in the blood, 643
Dextrose (grape sugar), 577, 601
,, acetates, 580
,, chloracetins of, 580
,, from diabetic urine, 583
,, ,, various sources, 582
,, reducing power of, 581
Diabetic sugar, 583
Diacetonalkamine, 780
Diacetonamine, 780
Diacetenylbenzene, 385
Diallyl, 220, 1002
,, dibromo-, 275
,, tetrabromide, 220
Diallylmethylcarbinol, 468, 1005
Diamidohydrin, 542
Diamyl, 141
Diamylene, 197, 1011
,, bromide, 198
Diarbutin, 689
Diargentic cyanurate, 122
Diatomic molecule, 44
,, radicle, 44
Dibenzoyl (benzil), 787
Dibenzoylbenzene ortho-, 386
,, para-, 385
Dibenzyl, 361
,, dibromo-, 361
,, dinitro-, 362
,, monobromo-, 361
,, trinitro-, 361

Dibenzylbenzene para-, 385
  ,, ortho-, 385
Dibenzylmethane, 363
Dibromethaldehydrol, 514
Dibromhydrin, 542
Dibromobenzenes, 302
Dibutyl, 141
Dichloracetone chloride, 159
Dichlorhydrin, 541
Dichlorethaldelhydrol, 514
Dichloroglycid, Reboul's, 205
Dicinnamene, 369
Diethyl, 138
Diethylbenzenes, 293
Diethylcarbinol, 450
Diethylenic dioxide, 678
Diethylic lactate, 889
Diethylmethylbenzene, 296
Diferrous dipotassic ferricyanide, 107, 1000
Diformylethylenediamide, 746
Digitalin, 693
Digitaliretin, 694
Dihydroanthracene, 367
Dihydroxyethylenamine, 677
Diiodhydrin, 543
Diisoamyl, 141
Diisobutol, 835
Diisobutyl, 141
Diisobutylene, 835, *note*
Diisopropylcarbinol, 455
Dill, oil of, 241
Dimethacrylates, 960
Dimethyl (ethane), 137
Dimethylacetylene, 219
Dimethylanthraquinone, 807
Dimethylallene, 220
Dimethylamidobenzoic, chloride, 786
Dimethylbenzene (xylene), 285
Dimethylbenzophenone, 363
Dimethylbutylmethane, 140
Dimethylcarbinol, 435
Dimethyldiethylmethane, 140
Dimethylethylene (butylene), 192
Dimethylethylethylene (hexylene), 196
Dimethylisobutylcarbinol, 455
Dimethylisopropylethylene, 197
Dimethylmetatrioxybenzene, 552
Dimethyltolane, 382
Dimesitylmethane, 363
Dinaphthalene, enneachloro-, 352
Dinaphthols, 537
Dinaphthyl, 388, 1004
  ,, dibromo-, 388
  ,, hexabromo-, 388
  ,, iso-, 388
  ,, ,, heptabrom-, 389
  ,, ,, tetrachlor-, 389
  ,, series of hydrocarbons, 388
  ,, tetranitro-, 388
Dinaphthylethane, 389
Dinaphthylethylene, 389, 1004
Dinaphthylmethane, 389
  ,, dibromo-, 389
  ,, tetranitro-, 389
Dinaphthyltrichlorethane, 389

Dioxyretistene, 382, 811
Dip (turpentine), 225
  ,, virgin, 226
Diphenols, 534
Diphenyl, 355
  ,, hexoxy-, 562
  ,, homologues of, 358
  ,, methyl-, 369, *note*
  ,, series, 355, 1004
  ,, substitution derivatives of, 356
Diphenylacetylene (tolane), 381
Diphenylbenzene, iso-, 385
  ,, para-, 385
Diphenylcarbinol, 503, 786
Diphenylchloromethanes, 361
Diphenyldiacetylene, 345, 285
Diphenyldichloromethane, 361
Diphenyldimethylethane, 363
Diphenylditolylmethane, 386
Diphenylenecarbinol, 503
Diphenylenemethane, or fluorene, 365
Diphenylenesulphone, 712
Diphenylenic disulphide, 711
  ,, oxide, 679
  ,, sulphide, 711
Diphenylethane, or dibenzyl, 361, 742
β-Diphenylethane, 362
  ,, haloid derivatives of, 362
α-Diphenylethylene, or stilbene, 366
β-Diphenylethylene, or isostilbene, 367
Diphenylethylene, haloid derivatives of, 367
Diphenylmethane, 360
  ,, nitro-derivatives of, 360
Dippel's oil, 258, 1003
Dipropargyl, 275
  ,, octobromide, 276
  ,, tetrabromide, 275
Dipropyl, 139
Dipropylcarbinol, 455
Direct combination, 43
Disacryl, 752
  ,, resin, 752
Discrimination of the gases, general remarks on, 29
Distillation, fractional, 7, 1000
  ,, in a current of steam, 10
Distilled waters, 239
Distyrolene, 369
Diterebene, 229, 232
α-Ditolyl, 361
Ditolyl, ortho-, 361
Ditolylacetylene, 382
α-Ditolylethane, 363
β-Ditolylethane, 363
Ditolylketone, 369
Ditolylmethane, 363
  ,, dibromo-, 363
  ,, dichloro-, 363
  ,, dinitro-, 363
Dixylyl, 363
Dodecane, normal, 141
Double cyanides, 98
Drying substances for analysis, 11

Dulcamaretin, 694
Dulcamarin, 694
Dulcitane, 683
Dulcite, or dulcitol, 558, 888
Dumas' method for combustions, 19
,, ,, determining nitrogen, 25
Dumasin, 788
Duplothioacetone, 662, 779
Durene (tetramethylbenzene), 294, 1003
Dyads, 42, 44
Dyslyte, 971

Ebonite, or vulcanite, 244
Elaïdin, 964
Elayl (ethylene), 183
Elæoptene, 223, *note*
Emodin, 808
Empirical formulæ, 35
Endecenylene, 222
Endecylene, 199
English turpentine oil, 234
Epibromhydrin, 543
Epichlorhydrin, 542
Epiiodhydrin, 543
Eremacausis, 72
Ericinol, 694, 699
Ericocin, 694
Erythrin, 528
Erythrol, or erythrite, 553
,, dibromhydrin of, 554
,, dichlorhydrin of, 553
Erythromannite (erythrol), 553
Erythrozym, 802
Essential oil of ajowan, 242
,, aniseed, 241
,, bay, 241
,, bergamot, 240
,, bitter almonds, 223
,, calamus, 297
,, camphor, 240
,, caraway, 241
,, cassia, 241
,, cinnamon, 241
,, cloves, 297
,, coriander, 241
,, cubebs, 297
,, cumin, 241
,, dill, 241
,, eucalyptus, 242
,, fennel, 241
,, galbanum, 242
,, garden cress, 223
,, juniper, 239
,, lavender, 242
,, lemons, 240
,, mace, 240
,, mustard, 223
,, neroli, 240
,, nutmeg, 240
,, orange peel, 240
,, patchouli, 297
,, peppermint, 242
,, petit grain, 240
,, rosemary, 242
,, rosewood, 297
Essential oil of sassafras, 241
,, savine, 239
,, spearmint, 242
,, spoonwort, 223
,, thyme, 242
,, watercress, 223
Essential oils, 222
Ethal, 457
Ethaldehyde (aldehyde), 727
,, action of acid amides on, 740
,, ,, amines on, 737
,, ,, ammonia on, 737
,, ,, halogens on, 733
,, ,, on hydrocarbons, 741
,, -ammonia, 737
chlor-, 742
,, compounds with acid sulphites, 734
,, condensation of, 732
,, dibrom-, 747
,, dichlor-, 743
,, haloid derivatives of, 742
,, higher homologues of, 747
,, met-, 731
,, par-, 731
,, parathio-, 742
,, polymerization of, 731
,, preparation of, 729
,, resin, 731
,, tribrom- (bromal), 747
,, trichlor- (chloral), 743
Ethaldehydrol chloracetin, 736
,, diacetin, 736
Ethane, 137
,, α-dibrom-, 156, 201
,, β-dibrom-, 156, 201
,, dibromotrichlor-, 744
,, α-dichlor-, 155, 200
,, β-dichlor-, 155, 200
,, α-dichlorocyan-, 176
,, dicyan-, 175
,, α-diiod-, 158, 213
,, β-diiod-, 158, 213
,, dinaphthyl-, 389
,, β-diphenyl-, 362
,, ditolyl-, 363
,, ethyl-β-diphenyl-, 363
,, haloid derivatives of, 155, 1001
,, hexabrom-, 202
,, hexachlor-, 156
,, iodobrom-, 157
,, iodochlor-, 157
,, isocyan-, 172
,, methyl-β-diphenyl-, 363
,, moniod-, 157
,, monobrom-, 156
,, monochlor-, 155
,, nitro-, 165
,, pentabrom-, 202
,, pentachlor-, 156
,, table of chlorinated derivatives of, 156
,, tetrabrom-, 202
,, tetrachlor-, 156

Ethane, tetraphenyl-, 390
,, tribrom-, 201
,, trichlor-, 156
,, trichlorodibromonitro-, 170
,, trichlorotrinitro-, 170
Ethene, 183 (*see* Ethylene)
Ethenedicymoquinone, 800
Ether, dichlor-, 672, 732
,, ethyl-allyl, 673
,, ethyl-benzyl, 675
,, ethylic, 668
,, chlorinated derivatives of, 671
,, glyceric, 679
,, glycidic, 685
,, methyl-benzyl, 675
,, methyl-phenyl, 674
,, methylic, 667
,, monochlor-, 671
,, pentachlor-, 673
,, perchlorinated, 673
,, phenylic, 674
,, sulphuric, 668
,, tetrachlor-, 672
,, thioethylic, 706
,, trichlor-, 672
,, vinyl-ethyl, 1009
Ether-alcohols, 682
,, ,, from glycerol, 685
,, ,, from pyrogallol, 685, 1009
Ethereal salts, 59
,, ,, of acids of the active series, 841, 1012
Etherification, theory of, 841
Ethers, 55, 663
,, benzyl, 675
,, double, or mixed, 664, 679
,, mixed, 664, 679
,, preparation of, 663
,, simple, 664
,, thio-, 704
Ethine, 209
Ethionic acid, 189
,, anhydride, 189
Ethylacetylene, 219
Ethylbenzene, 284
Ethylbromobenzene, 321
Ethylcarbaminic, 172
Ethylcarbinol, 434
Ethyldimethylbenzene, 294
Ethyldimethylcarbinol, 194, 450
Ethyl-β-diphenylethane, 363
Ethylene (elayl, olefiant gas), 183
,, chlorobromo-, 202
,, compounds of, with chlorides, 189
,, dibrom-, 201, 213
,, dichlor-, 201, 212
,, diethyl ether, 680
,, diiod-, 202
,, dinaphthyl-, 389
,, dinitrosodibrom-, 177
,, α-diphenyl- (stilbene), 366
,, β-diphenyl- (isostilbene), 367
,, ethylphenyl-, 342
,, haloid derivatives of, 1002
,, methylphenyl-, 342
Ethylene, moniod-, 202, 213
,, monobrom-, 201
,, monochlor-, 200
,, phenethyl-, 343
,, phenyl- (cinnamene), 340
,, polymerization of, 190
,, preparation of, 186
,, tetrabrom-, 202
,, tetrachlor-, 201
,, tetraphenyl-, 391
,, tribrom-, 202
,, trichlor-, 201
Ethylenic bromide, 156
,, chloride, 155
,, ethylidenic dioxide, 678
,, iodide, 158
,, oxide, 676
,, sulphide, 712
Ethylethylene (butylene), 191
Ethylic acetate, 848
,, acetoacetate, 909
,, ,, action of alkalis on, 913
,, ,, ,, nitrous acid on, 915
,, ,, metallic derivatives of, 911
,, acetocupracetate, 911
,, acetolactate, 889
,, acetonitrosoacetate, 915
,, acetosodacetate, 911
,, acetoxysuccinate, 940
,, acrylate, 957
,, amidoformate (urethane), 879
,, bromide, 156
,, camphoronate, 978
,, carbonate (urethane), 879
,, ,, thio-derivatives of, 881
,, carbonate, 877
,, carbuvate, 928
,, chloride, 155
,, chlorocarbonate, 878
,, chloroformate, or chlorocarbonate, 878
,, cyanide, 171
,, cyanocarbonate, 878
,, cyanoformate, or cyanocarbonate, 878
,, dehydromucate, 998
,, desoxalate, 953
,, diacetosuccinate, 928
,, diacetoxysuccinate, 945
,, diethacetate, 907
,, diethacetonecarbonate, 907
,, disulphide, 708
,, ethacetate, 907
,, ethacetonecarbonate, 907
,, ethoxyacetoethoxyacetate, 917
,, ethoxypropionate, 889
,, formate, 847
,, ,, action of sodium on, 915
,, fumarate, 969
,, glycolate, or hydroxyacetate, 883
,, glyoxylate, or dihydroxyacetate, 902

Ethylic hydride, 137
,, iodide, 157
,, isosuccinate, 930
,, isovalerate, action of sodium on, 916
,, lactate, 889
,, malate, 940
,, maleate, 969
,, malonate, 1012
,, mucate, 951
,, mucobromate, 995
,, β-nitrosopropionate, 915
,, orthoformate, 823 *note*
,, oxalate, 923
,, oxide, or ether, 668
,, propionate, action of sodium on, 915
,, propiopropionate, 915
,, saccharate, 951
,, selenide, 713
,, succinate, 927
,, ,, action of alkali metals on, 928
,, succinopropionate, 929
,, succinosuccinate, 929
,, sulphide, 706
,, sulphydrate (mercaptan), 661
,, tartrate, 945
,, telluride, 714
,, tetrasulphide, 708
,, trichlorolactate, 744
Ethylidene diethyl ether (acetal), 680
,, dimethyl ether, 680
,, methyl ethyl ether, 680
Ethylidenedibenzamide, 740
Ethylideneurea, 741
Ethylidenic bromide, 156
,, chloride, 155
,, cyanide, 175
,, iodide, 158
Ethylisoamyl, 140
Ethylisobutyl, 140
Ethylmethylbenzene, 286
Ethylmethylcarbinol, 439
Ethylmethylethylene, 450
Ethylnaphthalene, 355
Ethylphenol, 493
Ethylphenyl, 284
Ethylphenylacetylene, 369
Ethylphenylethylene, 342
Ethylvinyl bromide (α-dibromotetrane), 161
Eucalin, or eucalyptose, 590
Eucalypton (melitose), 615
Eugenol, 241, 684
Eulyte, 971
Eupion, 139
Everitt's white salt, 93, 107

Fecula (starch), 616
Fennel, oil of, 241
Ferrous dipotassic ferricyanide, 107
,, ,, ferrocyanide, 107
Ferric cyanide, 102
,, formacetonitrate, 824
,, formonitrate, 824
,, succinate, 927
Ferricyanides, 102
,, table of, 106
Ferrocyanides, 102
,, table of, 104
Filling combustion tube, 17
Fixed oils, 222
Flavopurpurin, 806
,, diacetyl-, 807
,, triacetyl-, 807
,, tribromo-, 807
Fluavil, 246
Fluorene, 365
,, bromo-, dibromide of, 365
Formal (methylal), 680
Formates, 823
Formethylamide, 746
Formionitrile hydrochloride, 94
Formonetin, 698
Formulæ, empirical, 35
,, graphic, 44
,, molecular, 36
Fractional crystallization, 6
,, distillation, 7, 1000
,, precipitation, 6
,, saturation, 7
,, solution, 6
Frangulin, 694
Frankincense, common, 226
Fraxetin, 695
Fraxin or paviin, 694
Fucusaldehyde (fucusol), 767
Fucusamide, 767
Fucusine, 767
Fucusol, 767
Fulminates, 123
,, constitution of, 176
Fumaric chloride, 968
Furfuraldehyde (furfurol), 766, 1010
Furfuramide, 767
Furfurine, 767
Furfurol or furfuraldehyde, 766
Furfuryl compounds, constitution of, 996
Furnace, combustion, 13
Fusel oil, 445

Galactose, 585
Galbanum, oil of, 241
Galipot (white resin), 226
Gallotannin, 703
Gas-coke, 247
Gas combustion furnace, 13
Gaseous mixtures, analysis of, 32
Geissler's potash bulbs, 16
Gin, 432
Githagin (saponin), 701
Globularetin, 695
Globularin, 695
Glucose (grape-sugar), 577
,, artificial, 590
,, in the blood, 643
,, optical properties of, 578
Glucosides, 686, 1009
Glycerin (*see* Glycerol),
Glycerol, or glycerin, 537, 1007
,, amylic, 547

Glycerol, dibromhydrins of, 542
,, dichlorhydrins of, 541
,, diethylin of, 682, 685
,, distillation of, 538
,, fermentation of, 545
,, iodhydrins of, 543
,, monallylin of, 685
,, monochlorhydrin of, 541
,, monethylin of, 682, 685
,, phosphate, 540
,, preparation of, 538
,, produced by fermentation, 538
,, sodium-, 539
,, sulphate, 540
,, ethlylin of, 685
,, trinitrate, 540
Glycidamine, 542
Glycide, 682
Glycine (glycocoll), 866
Glycines or amido-acids, 864, *et seq.*
,, properties of, 865
Glycocine (glycocoll), 866
Glycocoll or glycine, 866
Glycogen, 641, 1009
Glycol, 509, 1006
,, chloromethyl-, 541
,, chloro-α-propylenic, 541
,, diethylenic, 513
,, dimethyl-, 516
,, dimethyl-α-butylenic, 517
,, dimethyldibutyl-, 517
,, dimethyldiisopropyl-, 517
,, dimethyldipropyl-, 517
,, ethyl-, 516
,, ethylisopropyl-, 516
,, isopropyl-, 516
,, methyl-, 515, 1006
,, methyl-α-propylenic, 515
,, monethylin, 683
,, octylenic, 517
,, α-propylenic, 514
,, β-propylenic, 515
,, propylmethyl-, 517, 1006
,, tetramethyl- (pinacone), 516
,, tetraisopropyl-, 517
,, tetraphenyl-, 786
,, tetrapropyl-, 517
,, triethylenic, 513
,, trimethyl-, 516
,, xylene-, 533
Glycolamide, 883
Glycolic bromhydrin, 512
,, chloracetin, 512
,, chlorhydrin, 511
,, monacetin, 510
Glycolide, 883
Glycols, 504
,, amylenic, 516
,, aromatic, 519
,, classification of, 506
,, methods of preparation, 505
,, polyethylenic, 512
,, properties of, 507
Glycyrretin, 695
Glycyrrhizin, 695, 1009

Glyoxal, or oxalic aldehyde, 768
Glyoxaline, 769
,, tribromo-, 769
Gold (*see* Aurous)
Grape sugar (glucose), 577
Graphic formulæ, 44
Gratioleretin, 695
Gratioletin, 695
Gratiolin, 695
Gratiosoleretin, 695
Gratiosoletin, 695
Gratiosolin, 695
Guaiacol (methoxycatechol), 683
Gum arabic, 652
,, British, 623
,, thus, 226
,, tragacanth, 654
Gums, 651
Gun cotton, 649
Gutta, 246
Gutta percha, 245

Halogen acids, action of, on carbon compounds, 82
Halogens, action of on carbon compounds, 78
Haloïd derivatives of acids of the succinic series, 934
,, ,, ,, the acetic series, 857
,, ,, cyanoparaffins, 176
,, ,, ethane, 155
,, ,, ethylene, 200
,, ,, hydrocarbons, 52
,, ,, methane, 151
,, ,, nitroparaffins, 169
,, ,, paraffins, 147
,, ,, propane, 158
,, ,, propylene, 203
,, ,, tetranes, 161
,, ethers, 52
,, phosphorus compounds, action of, on carbon compounds, 81
,, salts, 58
Helicin, 695, 1009
,, benzo-, 695, 699
,, monobrom-, 695
,, monochlor-, 695
,, tetracetyl-, 695
,, tetrabenzoyl-, 695
Helicoidin, 696
Helleboreïn, 696
Helleboresin, 696
Helleboretin, 696
Helleborin, 696
Heptaldehyde (œnanthol), 751
Heptane, haloid derivatives of, 163
,, dichlor-, 163
,, α-iso-, 140
,, monochlor-, 163
,, normal, 140, 1000
Heptanes, 140
Heptene (heptylene), 196
Heptylene (œnanthylene), 196, 1001
Heptylcarbinol, 456

Heptylic chloride, 163
Hesperetin, 696
Hesperidene, 240
Hesperidin, 696
Heterologous series, 63
Heveene, 244
Hexabromhexylene, 300
Hexadecane, 141
,, haloid derivatives of, 163
,, moniod-, 163
,, monobrom-, 163
,, monochlor-, 163
Hexads, 42
Hexahydroanthracene, 355
Hexahydrometaxylene, 791
Hexahydropyrene, 367
Hexaldehyde, isoprimay, 751
,, normal, 751
Hexamethylenamine, 725
Hexane, dibrom-, 163
,, dichlor-, 517
,, hexachlor-, 163
,, α-iso-, 140
,, β-iso-, 140
,, γ-iso-, 140
,, δ-iso-, 140
,, moniod-, 163
,, monochlor-, 162
,, normal, 139
,, tetrabrom-, 220
,, tetriod-, 220
Hexane glycines or leucines, 870
Hexanes, 139
Hexdecaldehyde (palmitic aldehyde), 751
Hexene (hexylene), 195
Hexoylene, 220, 1002
Hexoxydiphenyl, 562
β-Hexylbenzene, 296
β-Hexylcarbinol, 454
Hexylene (caproylene), 195, 1001
,, hexabrom-, 300
,, hexachlor-, 305
Hexylenic oxide, 679
Hexylic chloride, 162
,, iodide, 163
Hexylmethylcarbinol, primary, 456
Hofmann's gas furnace, 13
,, method for vapour densities, 36, 1000
Homocatechol monomethylin, 684
Homologous series, 50
Homologues of benzene, 278
,, ,, bromo-derivatives of, 322
,, ,, chloro-derivatives of, 318
,, ,, iodo-derivatives of, 322
Homopyrocatechin, 532
Humus, 646
Hydramides, 720
Hydranisoïn, 764
Hydranzotin, 881
Hydrazulmin, 89
Hydric argentic fulminate, 124
Hydric auricyanide, 102
,, cyanate, 116
,, cyanide, 90
,, platinocyanide, 114
Hydrobenzamide, 756
Hydrobenzoin, 535, 1006
,, iso-, 535
Hydrobryoretin, 690
Hydrocarbons, 49, 50
,, acetenylbenzene series, 343
,, acetylene series, 208
,, anthracene series, 370
,, benzene series, 246
,, benzylnapthalene series, 383
,, cinnamene series, 340
,, chrysene series, 386
,, cyano-derivatives of the, 52
,, dinaphthyl series, 388
,, diphenyl series, 355
,, general review of the, 391, 1004
,, haloid derivatives of the, 52
,, idrialene series, 390
,, isologous series of, 51
,, naphthalene series, 345
,, nitro-derivatives of the, 52
,, olefine series, 177
,, paraffin series, 126
,, pyrene series, 383
,, stilbene series, 364
,, terpene series, 222
Hydrocellulose, 650
Hydrochloric acid type, 69
Hydrocinnamide, 768
Hydrocœrulignone, 562, 800
Hydrocyanaldin, 738
Hydrogen, estimation of, in carbon compounds, 12
,, nascent action of, 75
,, substitution for, 78
,, type, 68
Hydrogratiosoleretin, 695
Hydrohexaglyoxal, 769
Hydronaphthaquinone, 534
Hydroparoxybenzoin, 763
Hydrophlorone, 533
,, dichloro-, 526
Hydropiperoïn, 765
Hydroquinone, or quinol, 525
,, haloid derivatives of, 525
,, monochloro-, 525
,, tetrabrom-, 526
,, tetrachlor-, 526
,, tribrom-, 526
,, trichlor-, 526
Hydrovanilloïn, 765
Hydroxethylenamine, 677

Idrialene, 390
,, series of hydrocarbons, 390
,, trinitro-, 390
Idrialite, 390
Idriaquinone, 390
Imidocaprylonitrile, 871
Imidocaprylimide, 871

Imides, acid, 59
India-rubber, or caoutchouc, 243
,, vulcanized, 244
Indic cyanide, 99
Inosol, or inosite, 560
Intercellular substance, 645
Inulin, 637
,, action of acids on, 640
Inuloïd, 641
Inverted sugar, 584
Iodine, determination of, in carbon compounds, 28
,, triacetate, 850
Iodoform, 154
Iridicyanides, 115
Iron salts (*see* Ferric and Ferrous)
,, cyanides, 102
Isoallylene, 218
Isoamylmethyl, 140
Isoamylic aldehyde, 750
,, hydride, 139
,, oxalate, 923
Isobutane, 138
Isobutylene, 138, 1001
Isobutylcarbinol, 445
Isobutylic carbamate, 880
,, cyanoformate, 879
,, oxalate, 923
Isobutylisoamyl, 141
Isobutyl-β-isoamyl, 141
Isobutylmethyl, 139
Isobutyric aldehyde, 749
Isocholesterin, 497
Isodiphenylbenzene, 385
Isodulcite, or isodulcitol, 555, 1007
α-Isoheptane, 140
α-Isohexane, 140
β-Isohexane, 140
γ-isohexane, 140
δ-Isohexane, 140
Isohydranisoïn, 764
Isohydrobenzoïn, 535
Isohydropiperoïn, 765
Isologous series, 51
Isomeric compounds, 41
Isomerism, insufficiency of the present theory of, 983
,, Van t'Hoff-Le Bel hypothesis, 983
Iso-orcin, 532
Isopentane, 139
Isophloretin, 699
Isophlorizin, 699
Isophorone, 600
Isoprene, 220
,, terpene from, 234
Isopropacetaldehyde, 750
Isopropylacetylene, 219
Isopropylbenzene, 286
Isopropylcarbinol, 438
Isopropyldimethylcarbinol, 454, 1005
Isopropylethylene, 193, 450
Isopropylethylmethylcarbinol, 562
Isopropylic bromide, 159
,, chloride, 158
,, iodide, 160
Isopropylmethylcarbinol, 450
Isopurpurin, 806
,, dibrom-, 806
Isostilbene, 367
Isoterebenthene, 230
,, dihydrochloride, 230
,, monohydrochloride, 230
Isotetraldehyde, 749
Isovaleric aldehyde, 750
,, cyanide, 853
,, peroxide, 856

JALAPIN, 696
Jalapinol, 697
Juniper, oil of, 239

KEKULÉ's benzene symbol, 338
Ketone dibenzyl-, 787
,, di-dimethylamidophenyl-, 786
,, dimethyl- (acetone), 778
,, dinaphthyl-, 788
,, diphenyl-, 786
,, diphenylene-, 789
,, ethylbenzyl-, 785
,, ethylphenyl-, 785
,, ethylenediethyl-, 789
,, isopropylbenzyl-, 786
,, isopropylphenyl-, 785
,, methylbenzyl-, 785
,, methylcinnamyl-, 789
,, methylnitrosoethyl-, 915
,, methylnitrosopropyl-, 915
,, methylnonyl-, 783
,, methylphenyl- (acetophenone), 785
,, methylphenethyl-, 785
,, methyl-tertiary-butyl-, 783
,, nitrosodimethyl, 915
,, paraditolyl-, 787
,, phenylbenzyl- (deoxybenzoïn), 787
,, phenylcymyl-, 787
,, phenylnaphthyl-, 787
,, phenylenediethyl-, 789
,, propylphenyl-, 785
,, tolylphenyl-, 786
Ketones, 60, 770
,, action of nitric acid on, 1010
,, aromatic, 785, 786
,, of the acetic series, 778, 783
,, formation of, 771, 1010
,, properties of, 774
Klumene (acetylene), 209

LACTAMIDE, 891
Lactates, 889
Lactide, 890
Lactin (milk sugar), 609
Lactocaramel, 610
Lacton (milk sugar), 609
,, acetates, 585, 611
,, inversion of, 610
,, metallic derivatives of, 610
,, octacetate, 610
,, reducing powers of, 611
Lactose (milk sugar), 609, 1008
Lactose or galactose, 585

α-Lactose, 586, 1008
β-Lactose, 586
Lactylurea, 739
Lævoglucose, 584
Lævulosan, 585
Lævulose, 584
,, calcium, compound of, 584
Laserol, 959 *note*
Laserpitin, 959 *note*
Laurene, 296
Lavender, oil of, 242
Lead salts (*see* Plumbic)
,, sugar of, 827
Lecanorin, 528
Lees, 942
Lemons, oil of, 240
Leucine, 870
Leucogallol, 549
Liebig's potash bulbs, 16
Light naphtha, 253
,, ,, constituents of, 253
Ligneous matter, 645
Lignite, destructive distillation of, 254
Ligustrin, or syringin, 702
Linnemann's apparatus, 9
Lime salts (*see* Calcic),
Limited oxidation, 72
Lonicerin, or xylostein, 704

MACE, oil of, 240
Magnesic platinocyanide, 113
,, trimethacetate, 833
Magnetic iron cyanide, 105
Mairogallol, 549
Malates, 940
Malonates, 925
Maltose or starch sugar, 612, 1008
Manna, 536
,, trehala-, 613
Mannite or manitol, 556, 585, 588, 655
,, dibromhydrin, 557
,, dichlorhydrin, 557
,, hexacetate, 557
,, hexanitrate, 557
Marignac's oil, 170
Marsh gas (methane), 133
,, series or paraffins, 50
,, or methane type, 70
Melampyrite (dulcitol), 558
Melene, 199
Meleziton or melezitose, 614
Melin (rutin), 700
Melitose or eucalyptose, 615
Menhaden oil soap, destructive distillation of, 257
Menthene, 221
Menthol, 242, 467
Menyanthin, 697
Menyanthol, 697
Mercaptan, or thioalcohol, 661
Mercaptans or thioalcohols, 54, 659
Mercurallylic iodide, 207
Mercuric cyanide, 100
,, fulminate, 124
,, oxycyanide, 101
Mercuric sulphocyanate, 120
Mesitol, 494
Mesityl oxide, 788
Mesitylene, 287
,, bromo-, 321
,, dichloro-, 319
,, dinitro-, 326
,, monochloro-, 319
,, nitro-, 326
,, oxy-, 494
,, tribromo-, 321
,, trichloro- 319
,, trinitro-, 326
Mesitylenes, chloro-, 319
Meta-, meaning of prefix, 303, *note*
Metacetone, 601, 788
Metachloral, 743
Metacresol, 491
Metacrolein, 753
Metaldehyde, 732
Metallic salts, 58
,, type, 63
Metameric compounds, 41
Metarabin, 651
Metethaldehyde, 732
Methaldehyde, 723
Methaldehydrol, 509
Methane, bromotrinitro-, 170
,, chloronitro-, 170
,, dibenzyl-, 363
,, dibromo-, 153
,, dichloro-, 151
,, dichlorocyanonitro-, 170
,, dichlorodinitro-, 170
,, dichloronitro-, 170
,, diiodo-, 154
,, dimesityl, 363
,, dinaphthyl-, 389
,, diphenylene-, 365
,, diphenyltolyl-, 386
,, ditolyl-, 363
,, haloid derivatives of, 151
,, moniodo-, 154
,, monobromo-, 153
,, monochloro-, 151
,, naphthylphenyl-, 383
,, nitro-, 164
,, phenylenediphenyl-, 387
,, series (paraffins), 50
,, tetrabromo-, 154
,, tetrachloro, 153
,, tetraiodo-, 154
,, tetranitro-, 109
,, tetraphenyl-, 390
,, tribromo-, 153
,, tribromonitro-, 170
,, trichloro-, 151, 1000
,, trichloronitro- (chloropicrin), 170
,, tricyano, 175
,, triiodo-, 154
,, trinitro-, 169
,, triphenyl-, 385
Methenylammonic chloride, 94
Methethacetaldehyde, 750
Methylal, 680

Methylalizarin, 807
Methylanthracene, 382
,, dibromo-, 382
Methylanthraquinone, 382, 807
Methylated spirit, 432
Methylbenzene, or toluene, 283
Methylcarbinol (alcohol), 425
Methylchloracetol, 158
Methyldiethylcarbinol, 454
Methyldiethylethylene, 197
Methyldiphenyl, 369
Methyl-β-diphenylethane, 363
Methyldipropylbenzene, 297
Methylenedimethyl ether, or methylal, 680
Methylenic bromide, 153
,, chloride, 151
,, iodide, 154
Methylethyl, or propane, 138
Methylethylene, 190
Methylethylethylene, 195
Methylic acetate, 847
,, acrylate, 957
,, alcohol, 422
,, aldehyde, 723
,, bromide, 153
,, chloride, 151
,, carbonate, 880
,, citrate, 953
,, cyanoformate, 879
,, fumarate, 969
,, hydrate, 422
,, hydride or methane, 133
,, iodide, 154
,, maleate, 969
,, oxalate, 923
,, oxide or ether, 667
,, selenide, 713
,, sulphide, 708
,, telluride, 714
Methylhexylcarbinol, 456
Methylnaphthalene, 354
Methylnitrosoethylketone, 915
Methylphenol (cresol), 491
Methylphenylcarbinol, 492
Methylphenylethylene, 342
Meyer's method for vapour densities, 1000
Microscope, use of, 4
Milk sugar, 585, 1008
Mineral naphtha, 146
Mixed types, 71
Molecular formula, 36
,, ,, distinguished from empirical formula, 39, 40
,, ,, relations of, to vapour density, 38
,, weight defined, 38
Molecule, monatomic, diatomic, &c., 44
Molecules distinguished from atoms, 42, 44
Monacetin, 676
Monads, 42, 44
Monatomic molecule, 44
,, radicle, 44
Monodichloracetic chloride, 859
Monochlorhydrin, 541
Mononitro-paraffins, 164
Mucilage, 654
Murrayetin, 697
Murrayin, 697
Mycon, or mycose, 613
Mycose (trehalose), 613
Myristicol, 240, 467
Myrosin, 697

NAPHTHA, coal-tar, 247, 252
,, light-, 253
,, mineral-, 146
Naphthalene, 345
,, acetylene-, 364
,, benzyl-, 383
,, chlorides of, 351, *et seq.*
,, constitution of, 346
,, dibromo-, 353
,, dichloride, 351
,, dichloro-, 352, 498
,, dicyano-, 354
,, dinitro-, 354, 502
,, dinitro-α-chloro-, 352
,, enneachlorodi-, 352
,, ethyl-, 353
,, homologues of, 354
,, isomeric substitution derivatives of, 348
,, methyl-, 344
,, moniodo-, 353
,, monobromo-, 353
,, monochloro-, 351, 352, 353, 498
,, tetrachloride of, 352
,, monocyano-, 354
,, mononitro-, 353
,, pentabromo-, 353
,, pentachloro-, 350
,, perchloro-, 352
,, phenyl-, 383
,, phenylene- (pyrene), 383
,, series of hydrocarbons, 345
,, tetrabromo-, 353
,, tetrachloride, 351, 562
,, tetrachloro-, 352
,, tetrahydride, 343
,, tetranitro-, 354
,, tribromo-, 352
,, trichloro-, 354
Naphthalenes, bromo-, 353
,, chloro-, 351, 1004
,, cyano-, 354
,, nitro-, 353
Naphthaquinol, 534
Naphthaquinone, 799, 800
,, dichloro-, 800
,, dioxy, 799
,, oxy-, 799
Naphthazarin, 799
Naphtherythrol 554,
Naphthol derivatives, constitution of, 501
Naphthols, 497
,, amido-, 499
,, diamido-, 500
,, diimido-, 500
,, dinitro-, 500
,, nitro-, 499

Naphthols, nitroso-, 499
,, oximido-, 500
Naphthonitrile, 354
Naphthylic cyanide, 354
Naphthylphenylmethane, 383
Naquet's rule, 47
Nascent hydrogen, action of, 75
Nataloïn, 808
Neroli, oil of, 240
Nickelous cyanide, 99
Nitric acid, action of, 82
Nitriles, properties of, 173
,, table of, 172
Nitro-derivatives of the hydrocarbons, 52
Nitroform, 167
Nitrogen, analysis of carbon compounds for, 22
,, Dumas' method of determining, 25
,, determination, by relative volumes, 26
,, ,, method of Will and Varentrapp, 23
Nitrolic acids, 167
Nitroparaffins, reactions of, 165
,, haloid-, 169
,, table of, 164
Nitroprussides, 110
Nitrosodimethylketone, 915
Nitrous acid, action of, 82
Nonanes, 141
Nonene (nonylene), 197
Nonylacetylene, 222
Nonylene, 197
Nutmeg, oil of, 240

Octane, haloid derivatives of, 163
,, moniodo-, 163
,, monobrom-, 163
,, monochlor-, 163
,, normal, 140
Octaneglycine, 870
Octylene, 1002
Octylic bromide, 163
,, chloride, 163
,, iodide, 163,
Œnanthol, 751
Œnanthylidene, 221
Oil, bone, 258
,, dead, 252
,, Dippel's, 258, 1003
,, fusel, 445
,, -gas, 191
,, Marignac's, 170
,, of turpentine, 225
,, ,, English, 234
,, ,, French, 226
,, rock, 146
Oils, drying and non-drying, 962
,, essential, 222 (*see* Essential Oils)
,, fixed, 222
,, volatile, 222
Oleates, 963
Olefiant gas (ethylene), 183
Olefines, 177
Olefines, formation of, 178
,, haloid derivatives of, 199
,, isomerism of, 182
,, polymerization of, 198
,, properties of, 180, 1001
Oleins, 964
Ononetin, 698
Ononin, 698
Onospin, 698
Optically active substances sp. rotatory power of, 569
,, active substances, constitution of, 989
Orange peel, oil of, 240
Orcin or orcinol, 527
,, constitution of, 530, 1006
,, dibromonitro-, 532
,, haloid derivatives of, 531
,, isomerides of, 532
,, moniod-, 531
,, monobrom-, 531
,, nitro-derivatives of, 531
,, pentabrom-, 531
,, pentachlor-, 531
,, tribrom-, 531
,, trichlor-, 531
,, triiod-, 531
,, trinitro-, 532
Orcinols, 519, 1006
Oreosolin, 959 *note*
Organic analysis, principle of, 11
,, ,, of a solid not containing nitrogen, 13
,, chemistry, 49
,, ,, distinction from inorganic, 1
,, compounds, nature of, 1
Organized bodies, 2
Organo-metallic compounds, 63
Ortho-, meaning of prefix, 303, *note*
Orthobenzyltoluene, 362
Orthocresol, 491
Orthodiethylbenzene, 293
Orthodimethylbenzene, 492
Orthodiphenylbenzene, 385
Oxalates, 922
Oxaldines, 721
Oxamide, 89
Oxidation limited, 72
Oxidizing agents, 72
,, ,, action of, 71, 72
Oxybenzene (phenol,) 475
Oxychrysazin, 807
Oxycymoquinones, 799
Oxymetaxyloquinone, 798
Oxypentaldin, 738
Oxytetraldin, 738
Oxytrialdin, 737

Palladiocyanides, 114
Palladious cyanide, 114
Pamlitane, 141
Para-, meaning of prefix, 303, *note*
Parabenzyltoluene, 362

Paracresol, 491
Paracyanogen, 89
Paradibenzoylbenzene, 385
Paradibenzylbenzenes, 385
Paradiethylbenzene, 293
Paradimethyldiphenyl (paraditolyl), 361
Paradiphenylbenzene, 385
Paraditolyl, 361
Paræsculetin, 687
Paraffin, 141
,, beechwood-, 143
,, decomposition of, by heat, 144
,, manufacture, 141
Paraffins, 50, 126
,, classification of, 132
,, constitution of, 130
,, cyano-derivatives of, 171, 176
,, ,, ,, table of, 172
,, haloid derivatives of, 147, 162
,, ,, nitro-derivatives of, 169
,, homologous, table of, 134
,, isocyano-, table of, 173
,, isomeric, table of, 134
,, isomerism of, 132
,, modes of formation of, 127
,, nitro-derivatives of, 164, 1001
,, perchlorination of, 1000
Paraglobularetin, 695
Paraldehyde, 731
,, constitution of, 717
Paramylon, 635
Paranthracene, 377
Parapropylmethylbenzene (cymene), 289
Pararabin, 651
Parathioethaldehyde, 742
Paratolylphenyl, 369
Parethaldehyde, 731
Paridin, 698
Paridol, 698
Paristyphnin, 698
Partial saturation, 46, 47
Patchouli, oil of, 297
Paviin, or fraxin, 694
Peat, destructive distillation of, 257
Pectinose, 589
Pectous substances, 654
Pentads, 42
Pentaldehyde, normal, 750
,, iso-, 750
Pentane, dibromo-, 193
,, dichloro-, 162
,, iso-, 139
,, monochloro-, 162
,, normal, 139
,, tetrabromo-, 220
Pentaneglycines, 869
Pentanes, 139
,, haloid derivatives of, 162
Pentene, 193
Pentylene, 193
Peppermint, oil of, 242
Perissads, 47
Perry, 433
Persulphocyanogen, 120
Petit grain, oil of, 240
Petroleum, Rangoon, 146
,, American, 146
Peucedanin, 959 *note*
Phaseomannite (inosol), 560
Phenaldols, 760
Phenanthraquinol, 537, 811
Phenanthraquinone, 378, 811, 1011
Phenanthrene, 377
,, constitution of, 379, 1004
,, dibromide, 379
,, dibromo-, 379
,, dinitro-, 379
,, monobromo-, 379
,, mononitro-, 379
,, tetrahydro-, 361
,, tribromo-, 379
Phenanthrenehydroquinone, 537
Phenanthrimidoquinone, 811
Phenethaldehyde, 1010
Phenol (carbolic acid), 475
,, amidodinitro- (picramic acid), 478
,, amidosulpho-, derivatives of, 483
,, benzyl-, 503
,, derivatives, constitution of, 485
,, diamido-, 478
,, diamidonitro-, 478
,, dichloro-, 480
,, diiodo-, 481
,, dinitro-, 476
,, dinitrometabromo-, 334
,, ethyl-, 493
,, haloid nitro-derivatives of, 482
,, ,, sulpho-derivatives of, 483
,, metabromo-, 481
,, metachloro-, 480
,, metanitro-, 476
,, metiodo-, 481
,, methyl- (cresol), 491
,, nitro-derivatives of, 476
,, nitroso-, 477
,, nitrosulpho-derivatives of, 483
,, orthamido-, 478
,, orthiodo, 481
,, orthobromo-, 481
,, orthochloro-, 480
,, orthonitro-, 476
,, paramido-, 477, 478
,, parabromo-, 481
,, parachloro-, 480
,, paraethyl-, 493
,, paraiodo-, 481
,, paranitro-, 476, 478
,, paraphenyl, 502
,, pentachloro-, 480
,, tetrabromo-, 481, 1005
,, tribromo-, 481
,, triiodo-, 481
,, trinitro- (picric acid), 476
Phenols, 468, 1005
,, amido-, 478
,, bromo-, 481, 1005
,, chloro-, 480
,, dihydric (orcinols), 519
,, iodo-, 481
,, methods of preparing, 470, 1005

Phenols, nitro-, 476
,, properties of, 472
,, propyl-, 1006
Phenoquinone, 446, 797, 1005, 1010
Phenose, 559
Phenyl, 355 (*see* Diphenyl)
Phenylacetylene, 343
Phenylbenzene, 355 (*see* Diphenyl)
Phenylbutylene, 342, 343
Phenylcarbamine, 328
Phenylcarbinol, 490
Phenylchloropropylene, 342
Phenylcyanopropylene, 342
Phenylethylene, 340 (*see* Cinnamene)
Phenylethylic acetate, 492
Phenylglycerol, 552
Phenyliodopropylene, 342
Phenylmercaptan, 662
Phenylnaphthalene, 383
Phenylpropylcarbinol, 494
Phenylpropylene, 342
Phenylenediphenylmethane, 387
Phenylenenaphthalene or pyrene, 383
Phenylenic sulphides, 712
Phenylic acetate, 847
,, bromide, 300
,, carbonate, 818
,, chloride, 305
,, cyanide, 327
,, disulphide, 713
,, hydride (*see* Benzene),
,, iodide, 311
,, isocyanide, 328
,, succinate, 928
,, sulphide, 711
,, sulphydrate, 662
Phillygenin, 698
Phillyrin, 698
Phloramine, 551
Phloreïn, 551
Phloretin, 698
,, nitro-, 699
,, tetrabromo-, 699
Phlorizin, 698
Phloroglucin or phloroglucol, 550, 1007
,, constitution of, 551
,, tribromo-, 551
,, trinitro-, 551
Phlorol, 493
Phlorone (xyloquinone), 798
Phlorozeïn, 698
Phorone, 789
Phosphonic acids, 57
Phosphorus, determination of, in carbon compounds, 26
Phthalaldehyde, 770, 1010
Phycite (erythrol), 553
Phylomelin (rutin), 700
Physiological Chemistry, 2
Picoline, 754
Picroerythrin, 528
"Pieces" (sugar), 596
Pinacolic alcohol, 453
Pinacolin, 783
Pinacone, 517
Pinipicrin, 699
Pinite, 555
Piperonal, 765
Pitch, coal tar-, 252
Platinicyanides, 114
Platinocyanides, 113
Plumbic acetate, 827
,, acrylate, 956
,, cyanide, 99
,, formates, 823, 824
,, glycolate or hydroxyacetate, 883
,, malate, 940
,, propionate, 828
,, sulphocyanate, 119
Polarimeter, Jellett-Cornu's, 572
Polaristrobometer, Wild's, 572
Polarizing apparatus, 569
,, ,, Broch's, 587, *note*
Polyatomic molecule, 44
Polygalin (saponin), 701
Polymeric compounds, 41
Polymerization of ethylene, 190
,, olefines, 198
Populin, 699
Porter, 433
Potash bulbs, 16
Potassic acetates, 826
,, angelate, 960
,, argentic cyanide, 100
,, auricyanide, 102
,, aurocyanide, 101
,, chlorodioxyquinonesulphonate, 796
,, chromicyanide, 112
,, cobalticyanide, 112
,, cobaltocyanide, 111
,, cyanate, 117
,, cyanide, 96
,, cyanurate, 122
,, dichloroquinoldisulphonate, 796
,, dimethacrylate, 960
,, dioxyquinonedisulphonate, 786
,, β-ethoxypropionate, 889
,, euthiochronate, 796
,, ferricyanide, 105
,, ferrocyanide, 102
,, ferrous cyanide, 102
,, iridicyanide, 115
,, isocyanate, 118
,, isosulphocyanate, 119
,, manganicyanide, 112
,, manganocyanide, 112
,, mercuric cyanide, 101
,, orthoformate, 824
,, osmiocyanide, 113
,, platinichlorocyanide, 114
,, platinicyanide, 114
,, platini-iodocyanide, 114
,, platinocyanide, 113
,, pyromeconate, 999
,, quinoldisulphonate, 796
,, sulphocyanate, 118, 119
,, tartrates, 944
,, tetroxybenzenedisulphonate, 796
,, thiocronate, 796
,, thiosuccinate, 928

Potassic trichloroquinolsulphonate, 796
,, trimethacetate, 833
Precipitation, fractional, 6
Proof spirit, 427
Propaldehyde, 747
Propane, 138
,, bromiodo-, 161
,, bromonitro-, 166
,, chloriodo-, 161
,, chlorobromiodo-, 161
,, chlorodibromo-, 160
,, chloromonobromo- 161
,, dibromo-, 159, 206, 1001
,, dibromodichloro-, 204, 205
,, dibromonitro-, 167
,, dichloriodo-, 161
,, dichloro-, 158
,, diacyano-, 175
,, diiodo-, 161
,, dinitro-, 168, 169, 1001
,, hexachloro-, 159
,, iodochloro-, 204
,, moniodo-, 160
,, monobromo-, 159
,, monochloro-, 158
,, pentachloro-, 159
,, tetrabromo, 160, 218
,, tetrachloro-, 159
,, tribromo-, 160, 206
,, trichloro-, 159, 205
,, tricyano-, 175
,, trinitro-, 169
Propargylene, 222
Propargylic bromide, 468
,, chloride, 468
,, iodide, 468
Propene (propylene), 190
Propheterin, 699
Prophetin, 699
Propine (allylene), 217
Propionitrile, 172
Propylacetylene, 219
Propylbenzene, 286
Propylcarbinol, 438
Propyldiethylcarbinol, 457
Propyldimethylbenzene, 296
Propyldimethylcarbinol, 454
Propylene, 190
,, chlorobromo-, 206, 1002
,, dibromo-, 206
,, dibromodichloro-, 206
,, dichloro-, 204, 516, 753
,, diiodo-, 208
,, moniodo-, 207
,, monobromo-, 205
,, monochloro-, 203
,, α-phenyl-, 342
,, β-phenyl- (allylbenzene), 342
,, phenylchloro-, 342
,, phenylcyano-, 342
,, phenyliodo-, 342
,, polymerization of, 191
,, tetrabromodichloro-, 207
,, tribromodichloro-, 207
,, triiodo-, 208
Propylenic bromide, 159
,, chloride, 158
,, cyanide, 175
,, iodide, 161
,, oxide, 678, 1009
Propylethylcarbinol, 453
Propylethylene, 193
Propylethylmethylcarbinol, 562
Propylic alcohol (*see* Alcohol, propylic)
,, bromide, 159
,, carbamate, 880
,, chloride, 158
,, hydride, or propane, 138
,, iodide, 160
,, oxalate, 923
Propylidenic bromide, 159
,, chloride, 158
Propylmethylbenzene, 289
Propylmethylcarbinol, 449, 1005
Propylmethylmetatrioxybenzene, 552
Propylpseudonitrol, 168
Proximate analysis, 4
Prussian blue, 107
,, ,, basic, 107
,, ,, commercial, 109
,, ,, soluble, 108
,, ,, Turnbull's, 109, 1000
,, green (magnetic cyanide), 105
Prussiate of potash, red, 105
,, ,, yellow, 102
Pseudobutylic hydride, 138
Pseudocumene, 288
,, bromo-, 321
,, nitro-, 326
,, tribromo-, 321
,, trinitro-, 326
Pseudocumenol, 1006
Purpurin, 805
,, iso-, 806
Purpuroxanthin, 804
,, diacetyl-, 804
,, dibromo-, 804
,, dinitro-, 804
Pyrene, 383
,, constitution of, 384
,, dibromo-, dibromide of, 384
,, dinitro-, 385
,, hexahydro-, 369
,, mononitro-, 384
,, tetranitro-, 385
,, tribromo-, 384
Pyrenequinone, 384, 811
Pyrocatechin, or catechol, 524
Pyrogallol (pyrogallic acid), 547, 1007
,, constitution of, 552
,, ether-alcohols, 1009
,, tribromo-, 548
Pyrogalloquinone, 797
Pyroxylic spirit (methylic alcohol), 422
Pyroxylin, or gun cotton, 649

QUANTIVALENCE, 42
Quercite, or quercitol, 554
,, constitution of, 560
,, pentacetate, 555

Quinhydrone, 797, 1010
Quinizarin, or chinizarin, 376, 804
Quinol, or hydroquinone, 525
,, constitution of, 812, 1011
,, diacetyltetrachloro-, 796
,, dichlorodioxy-, 796
,, dimethyl-, 533
,, dinitro-, 689
,, methylpropyl-, 533
,, monomethylin, 684
,, naphtha-, 534
Quinone, or benzoquinone, 794
,, dichloro-, 795
,, dichlorodioxy- (chloranilic acid), 796
,, haloid derivatives of, 795
,, methyl- (toluquinone), 798
,, methylpropyl- (thymoquinone), 798
,, monochloro-, 795
,, oxydimethyl-, 178
,, pheno-, 797
,, pyrogallo-, 797
,, tetrabromo-, 796
,, tetrachloro-, 796
,, trichloro-, 796
Quinones, 793
Quinova bitter, 699
,, sugar, 699
Quinovin, 699

RADICLE, 64, 65
Radicles, compound, 64
,, Gerhardt's theory of, 65
,, monad, 66
,, monatomic, &c., 44
Raffinose, 603
Reagents, action of, on carbon compounds, 71
Reducing agents, 75
,, ,, action of, 75
Resin soap, 239
Resins, 239
Resorcinol, or resorcin, 521
,, diazo-, 523
,, dinitroso-, 523
,, haloid derivatives of, 522
,, iodo-, 523
,, monomethylin, 684
,, mononitro-, 523
,, pentabromo-, 523
,, pentachloro-, 523
,, tribromo-, 523
,, trichloro-, 523
,, trinitro-, 523
Resorquinone, 798
Retene, 382
Retistene, 382
Rhamnegin, 700
Rhamnetin, 700
Rhamnin, 700
Rhamnogenin 700
Rhinanthin, 700
Rhodicyanides, 115
Rhodonates (thiocyanates), 118
Robinin, 700
,, sugar, 700
Rochelle salt, 944
Rock oil (naphtha), 146
Rosemary, oil of, 242
Rosewood, oil of, 297
Rosin, 226
Rubian, 802
Ruficoccin, 691
Rum, 432
Rutheniocyanides, 113
Rutin (melin), 700
Rutylene, 221

SACCHARINE group, or Saccharons, 592
Saccharon, or cane sugar, 593, 1008
Saccharons, 592
,, artificial, 615
Saccharose, (cane sugar), 593
Safrol, 241
Sago, 622
Salicin, 701
,, benzoyl-, or populin, 699
,, bromo-, 701
,, chloro-, 701
,, dichloro-, 701
,, perchloro-, 701
,, sodium-, 701
,, tetracetyl-, 701
Salicylic aldehyde, or salicylol, 760
,, aceto-, 762
,, bromo-, 761
,, chloro-, 761
,, methyl-, 761
Saligenin, or saligenol, 527
,, bromo-, 701
,, dichloro-, 527
,, monochloro-, 527
Saligenols, 519
Salts, ethereal, 59
,, haloid, 58
,, metallic, 58
Sapogenin, 701
Saponin, 701
Sarcolactide, 892
Sassafras, oil of, 241
Saturated compounds, 50
,, molecule, 44, 67, *note*
Saturation, fractional, 7
Savine, oil of, 239
Scammonium, 696
Seignette salt, 944
Selenaldine, 739
Senegin (saponin), 701
Separation by solvents, 4
Series, heterologous, 63
,, homologous, 50
,, isologous, 51
Sesquiterpenes ($C_{15}H_{24}$), 297, 1004
Silver acetylide, 214, 215
,, dicyanimide, 118
,, salts (*see* Argentic)
Sinalbin, 702, 1009
Sinapisine sulphate, 702
Soap, Menhaden oil, 257

Soap, resin-, 239
Socaloïn, 808
Sodic acetates, 826
,, acrylate, 956
,, cobalticyanide, 112
,, hydracrylate, or hydroxypropionate, 886
,, hydroxybutyrates, 895
,, lactates, 889
,, manganocyanide, 112
,, nitroprusside, 111
,, orthoformate, 824
,, tartrate, 944
,, zincic cyanide, 99
Sodium nitroethane, 165
Solanicine, 702
Solanidine, 702
Solanine, 702
Solution, fractional, 6
Solvents, use of, in proximate analysis, 4
Sorbin, or sorbinose, 589
Sorbite, 559
Spearmint, oil of, 242
Specific rotatory power, 572
Spirit of wine (ethylic alcohol), 425
,, ,, methylated, 432
,, ,, proof-, 427
Spirits, 432
Starch, 616, 1008
,, acetates, 624
,, action of acids on, 633
,, ,, malt extract on, 625
,, gelatinized, 623
,, grains, composition of, 617
,, ,, formation of, 618
,, nitro-derivatives of, 625
,, -paste, 623
,, potato-, 620
,, properties of, 622
,, rice-, 621
,, soluble, 623
,, sugar (amylon), 612
,, torrefied, 623
,, wheat-, 621
Stearopten of oils, 223 *note*
Stilbene, (toluylene), 366
,, bromo-, 367
,, dibromide, 361
,, homologues of, 368
,, iso-, 367
,, tribromo-, 367
Stockholm tar, 255
Stout, 433
Strontic acetate, 826
Struthin (saponin), 701
Styrol (cinnamene), 340
Styrolene (cinnamene), 340
Suberone, 933
Substitution compounds, 78, 79
,, in the phenol series, 489
Succinates, 927
Succinic chloride, 927
Sucrodextrose (glucose), 577
Sucrolævulose (lævulose), 584
Sucrose (cane sugar), 593
Sugar, action of acids on, 600
,, ,, bases on, 601
,, ,, heat on, 597
,, beetroot, 594
,, cane, or saccharon, 593, 1008
,, 'crushed,' 596
,, diabetic, 583
,, effect of, on polarized light, 597
,, estimation of, 605
,, fermentation of, 604
,, in the blood, 643
,, ,, urine, 583
,, inversion of, 601
,, -lime, 598
,, manufacture of, 593
,, metallic derivatives of, 598
,, milk- or lacton, 608, 1008
,, of lead, 827
,, quinova-, 699
,, reducing power of, 605
,, refining, 595
,, robinin-, 700
,, rotatory power of, 597
,, separation of potash salts from, 596
,, starch-, or amylon, 612, 1008
Sulphine, dibutyl-, 814
,, diethyl-, 814
,, diisobutyl-, 814
,, diisoamyl-, 814
,, dimethyl-, 814
,, ethylamyl-, 814
,, methylethyl-, 814
,, paratolydi-, 814
,, phenyldi-, 814
Sulphines, 706, 814
Sulphinic acids, 57
Sulpho-acids, 57
Sulphobenzid, 815
,, oxy-, 815
Sulphocarbonates, 880
Sulphocyanates, 118
Sulphone, dibutyl-, 815
,, dichlorophenyl-, 815
,, diethyl-, 815
,, dimethyl-, 815
,, diphenyl- or sulphobenzid, 815
,, ditolyl-, 815
,, naphthyl-, 815
,, paradioxyphenyl-, 815
,, phenylnaphthyl-, 815
Sulphones, 706, 814
Sulphonic acids, 57
Sulphur, determination of, in carbon compounds, 26
,, diethmethiodide, 710
,, dimethyl, compounds of, 710
,, ethmethiodide, 710
,, ethylmethylethyl, compounds of, 710
,, triethiodide, 710
,, trimethiodide, 709
Synanthrose, 636, 1009
Synthesis of carbon compounds, 1
Syringenin, 702
Syringin (ligustrin), 702

TABLE of acetylene series, 208
,, acid anhydrides of the acetic series, 855
,, acids of the acetic series, 20, 840, 1012
,, ,, ,, acrylic series, 953
,, ,, ,, glycolic or lactic series, 873
,, ,, ,, maleic series, 967
,, ,, ,, succinic series, 918
,, alcohols of the benzene series, 469, 1005
,, ,, ,, ethylic series, 405, 458, 1005
,, aldehydes of the acetic series, 722
,, ,, ,, benzene series, 755
,, amines, 61
,, amylic alcohols, 444
,, anthracene series of hydrocarbons, 370
,, bases from bone oil, 258
,, benzene series of hydrocarbons, 278, 1003
,, ,, ,, substitution derivatives of, 337
,, brominated derivatives of propane, 159
,, ,, ,, tetrane, 159
,, ,, ,, toluene, 320
,, bromophenols, 481
,, bromotoluenes, 320
,, carbamines, 173
,, chlorethanes, 156
,, chlorinated derivatives of ethane, 156
,, ,, ,, propane, 158
,, ,, ,, toluene, 318
,, chlorobromopropanes, 160
,, chlorophenols, 480
,, chloropropanes, 158
,, chlorotoluenes, 318
,, cinnamene series of hydrocarbons, 340
,, coal tar products, 251, 1003
,, cyanic acid polymerides, 126
,, cyanoparaffins, 172
,, dihaloïd derivatives of benzene, 337
,, dinaphthyl series of hydrocarbons, 388
,, diphenyl derivatives, 355, 357
,, double cyanides, 115
,, ethereal salts of acids of the acetic series, 846
,, ethers, 667
,, ferricyanides, 106
,, ferrocyanides, 104
,, haloid glycols, 518
,, ,, cyano-derivatives of the paraffins, 176
Table of haloid derivatives of the paraffins, 150
,, ,, ,, methane, 151
,, ,, nitro-derivatives of the paraffins, 169
,, ,, ,, phenol, 483
,, heptylic alcohols, 454
,, hexylic alcohols, 452
,, homologous series, 64
,, ,, paraffins, 134
,, homologues of benzene, 278
,, hydrocarbons of the acetylene series, 208
,, ,, anthracene series, 370
,, ,, benzene series, 278
,, ,, cinnamene series, 340
,, ,, dinaphthyl series, 388
,, ,, diphenyl series, 355
,, ,, idrialene series, 390
,, ,, naphthalene series, 345
,, ,, olefine series, 184
,, ,, paraffin series, 134
,, ,, pyrene series, 383
,, ,, stilbene series, 364
,, ,, from Menhaden oil soap, 257
,, iodophenols, 482
,, isocyano-paraffins, 173
,, isologous hydrocarbons, 51
,, ,, paraffins, 134
,, ketones of the acetic series, 784
,, ,, aromatic series, 785, 786
,, mercaptans, or thioalcohols, 659
,, metallocyanic radicles, 115
,, monhydroxy-derivatives of acids of the acetic series, 873
,, mononitrotoluenes, 325
,, nitrites, 172
,, nitro-haloid derivatives of benzene, 331, 332
,, nitroparaffins, 164
,, nitrophenols, 477
,, nitrotoluenes, 325
,, octylic alcohols, 456
,, olefines, 178, 184
,, organo-metallic compounds, 63
,, paraffins, 134
,, pentylic alcohols, 444
,, phenols, 469, 1005
,, polymerides of cyanic acid, 126
,, pyrene series of hydrocarbons, 383
,, reactions of sodium nitro-paraffins, 165
,, stilbene series of hydrocarbons 364
,, substitution derivatives of benzene, 337
,, thioalcohols, 659
,, thioethers, 704
Tampicin, 703
Tannins, 703
Tapioca, 622

Tar, coal-, 247
,, compounds present in, 251, 1003
,, distillation of, 252
,, Stockholm-, 255
,, wood-, 254
Tartar, 942
,, emetic, 944
Tartrates, 944
Terebene, 231, 1002
,, monohydrochloride, 232
,, polymerization of, 232
Terebenthene, 226
,, austra-, 234
,, compounds with haloid acids, 227
,, dihydrochloride, 228
,, hydrobromide, 229
,, hydrochloride, 229
,, hydriodide, 229
,, iso-, 230
,, ,, dihydrochloride, 230
,, ,, monohydrochloride, 230
,, polymerization of, 229
Terecamphine, active, 232
,, inactive, 233
Terpene from isoprene, 234
,, hydrochlorides, 1002
,, monohydrates, 1003
Terpenes, 222
,, artificial, 224, 1002
,, compounds of, with water, 236
,, constitution of, 290
,, from aurantiaceæ, 240
,, ,, caoutchouc, 244
,, ,, labiatæ, 242
,, ,, lauraceæ, 240
,, ,, myristiceæ, 240
,, ,, umbelliferæ, 241
,, natural, 225, 238
,, nitroso-, 236, 1003
,, oxidation, products of, 237
,, sesqui-, ($C_{15}H_{24}$), 297
,, tetrachloro-, 236
Terpentine hydrate, 237
Terpin, 236
Terpinol, 228
Tetrads, 42, 45
Tetrahydrometaxylene, 221
Tetrahydrophenanthrene, 361
Tetraldehyde (butyraldehyde), 747
,, normal, 747
,, trichloro-, 749
Tetraldol (oxybutyric aldehyde), 748
Tetramethylallene, 221
Tetramethylbenzene, 294
Tetramethylethane, 140
Tetramethylmethane, 139
Tetrane, dibromo-, 161
,, haloïd derivatives of, 161
,, moniodo-, 161
,, monobromo-, 161
,, monochloro, 161
,, normal, 138
,, tetrabromo-, 162, 219
Tertane, tribromo-, 162
Tetraneglycine, 869
Tetraphenol, 993
Tetraphenylethane, 390
Tetraphenylethylene, 391
Tetraphenylglycol, 786
Tetraphenylmethane, 390, 1004
Tetraterebenthene, 229
,, dihydrochloride, 230
,, monohydrochloride, 230
Tetroxydiphenoquinone, 800
Tetrylene (butylene) 191
Theory of compound radicles, 64
Thialdines, 721, 739
Thioalcohol or mercaptan, 661
Thioalcohols (mercaptans), 54, 659
Thiobenzaldehydes, 759
Thiocarbamates, 881
Thiocarbonates, 880
Thiocarvacrol, 662
Thiocresols, 662
Thiocyanates, 118
Thioethers, 55, 704
Thiofurfurol, 767
Thioglycerol, 663
Thioglycol, 662
Thiomethaldehyde, 725
Thionaphthols, 662
Thiophenol, 662
,, parabromo-, 662
Thioquinol, 663
Thioresorcinol, 663
Thiothymol, 662
Thiourea, 119
Thus, gum-, 226
Thyme, oil of, 242
Thymene, 242
Thymolhydroquinone or thymoquinol, 553
Thymoïlol (thymoquinol), 533
Thymol, 242, 494
,, dibromo-, 494
,, dinitro-, 494
,, pentabromo-, 494
,, pentachloro-, 494
,, trinitro-, 494
Thymoquinone, 798
,, oxy-, 799
Thujetin, 703
Thujigenin, 703
Thujin, 703
Tolane, 381
,, bromides, 382
,, dibromide, 381
,, dichloride, 382
,, dimethyl-, 382
,, tetrachloride, 382
Toluene, 283
,, chloro-, derivatives of the homologues of, 318
,, diorthodinitro-, 325
,, metabromo-, 319
,, metanitro-, 324
,, monobromo-, 320
,, nitro-haloid, derivatives of, 332, 1004

Toluene, orthobromo-, 320
,, orthochloro-, 313
,, orthonitro-, 324
,, orthoparadinitro-, 325
,, parabromo-, 320
,, parachloro-, 313
,, paranitro-, 324
Toluenes, bromo-, 319
,, chloro-, 311
,, dibromo-, 320
,, dichloro-, 314
,, dinitro-, 324
,, heptachloro-, 317
,, hexachloro-, 317
,, monobromo-, 319
,, monochloro-, 313
,, nitro-, 324, 1004
,, pentachloro-, 316
,, tetrachloro-, 316
,, tribromo-, 320
,, trichloro-, 314
,, trinitro-, 325
Toluhydroquinone, 533
Toluquinone, 798
,, tetrachloro-, 798
Toluylene, 366 (*see* Stilbene)
Toluyl hydrate, 503
Tolylcarbinol, 492
Tolylphenyl, para-, 369
Tolylphenylcarbinol, 503
Treacle, 594, 596
Trehala manna, 613
Trehalose (mycose), 613
Triacetonalkamine, 780
Triacetonamine-, 780
,, nitroso-, 780
Triads, 42, 45
Triamylenic dibromide, 222
Triargentic cyanurate, 122
Triatomic molecule, 44
,, radicle, 44
Tribromethaldehydrol, 514
Tribromhydrin, 160
Tribromobenzenes, 302
Tribromoresorquinone, 523
Trichloracetic chloride, 859
Trichlorethaldehydrol (chloral hydrate) 513
Trichlorhydrin, 159
Trichlorobutaldehydrol, 516, 747
Trichlorobutyric aldehyde, 749
Trichlorotetradehydrol, 516, 749
Triethylbenzene, 296
Triethylcarbinol, 455
Triethylmethane, 140
Triferrous ferricyanide, 109
Trihydroxethylenamine, 677
Triisobutylene, 193
Trimethylbenzene, 287
Trimethylcarbinol, 439
Trimethylethylene, 194
Trimethylethylmethane, 140
Trimethylmethane, 138
Trioxymetaxylene, 552
Trioxynaphthalene, 552
Triphenylbenzene, 390
,, monobromo-, 390
,, trinitro-, 390
Triphenylcarbinol, 385, 504
Triphenylchloromethane, 386
Triphenylmethane, 385, 1004
Turpentine, collection of, 225
,, larch, 239
,, oil of, English, 225, 234
,, ,, French, 225, 226
,, Strasburg, 239
,, Venice, 239
Turpethin, 704
Type, ammonia, 69
,, hydrochloric acid, 69
,, hydrogen, 68
,, marsh gas, 70
,, metallic, 68
,, water, 69
Types, chemical theory of, 67
,, mixed, 71
Typical hydrogen, 71
Tyrosine, 869

ULTIMATE analysis, 4, 11
Unsaturated compounds, 50
Urethane (ethylic carbamate), 879

VALENCY, change of, 47
Valeral or valeraldehyde, 750
Valerylenes, 219, 1002
Valylene, 223
,, dibromo-, 224
Vanillin, 685, 692, 764
Vapour density, Hofmann's method for, 36, 1000
,, ,, Meyer's method, 1000
Varrentrapp and Will's method for determining nitrogen 23
Vegetable mucilage, 654
,, parchment, 650
Veratrol, 682
Vinegar making, 824
Vinylic alcohol, 213
,, bromide, 201
,, chloride, 200
,, iodide, 202
Volatile oils, 222
Vulcanite or ebonite, 244

WAIFA or Chinese yellow, 700
Warren's still, 8
Water oven, 11
,, type, 69
Waters, distilled-, 239
Whisky, 432
Wine, spirit of (alcohol), 425
,, varieties of, 432
Wines, 432
,, strength of, 434
Wood, destructive distillation of, 254
,, spirit (methylic alcohol), 422
,, tar, 254

XANTHOGALLOL, 548

Xanthorhamnin, 700
Xenols or xylenols, 492, 1005
Xyloïdin, 625
Xylene, 285
Xylene, benzylmeta-, 363
  ,, benzylpara-, 363
  ,, bromometa-, 321
  ,, dichloro-, 319
  ,, dinitrometa-, 325
  ,, glycol, 533
  ,, meta-, 285
  ,, metatrioxy-, 798
  ,, monochloro-, 319
  ,, ortho-, 285
  ,, para-, 285
  ,, tetrabromo-, 321
  ,, trichloro-, 319
  ,, trinitrometa-, 326
  ,, trinitropara-, 325
Xylenes, bromo-, 321
Xylenes, chloro-, 318
  ,, constitution of, 321
  ,, nitro-, 325
  ,, separation of, 1003
Xylenols or xenols, 492, 1005
Xyloquinone (phlorone), 798
Xylosteïn, or lonicerin, 704

YELLOW, Chinese-, 700

ZANALOIN, 808
Zincic butyrate, 830
  ,, cyanide, 99
  ,, dimethethacetate, 834
  ,, hydracrylate or hydroxypropionate, 887
  ,, hydroxybutyrate, 895
  ,, isobutyrate, 830
  ,, lactate, 889
  ,, trimethacetate, 833

END OF SECTION I.

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